

# MEMBER INSIDE PLASMA TREATMENT CHAMBER, AND MANUFACTURING METHOD THEREFOR

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## Abstract of JP2001164354

**PROBLEM TO BE SOLVED:** To provide a member inside a plasma treatment chamber, excellent in plasma erosion resistance, and to provide an advantageous manufacturing method therefor.

**SOLUTION:** The surface of a base material is coated with a multilayered combined layer consisting of a metal film formed as an undercoat, an Al<sub>2</sub>O<sub>3</sub> film formed as an intermediate layer on the undercoat, and a Y<sub>2</sub>O<sub>3</sub> sprayed deposit formed as a topcoat on the intermediate layer.

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(54) 【発明の名称】 プラズマ処理容器内部材およびその製造方法

(57) 【要約】

【課題】 耐プラズマエロージョン性に優れるプラズマ処理容器内部材と、その有利な製造方法とを提案する。

【解決手段】 基材の表面が、アンダーコートとして形成された金属皮膜と、そのアンダーコート上に中間層として形成された  $Al_2O_3$  皮膜と、そしてその中間層上にトップコートとして形成された  $Y_2O_3$  溶射皮膜とからなる多層状複合層によって被覆されている。

## 【特許請求の範囲】

【請求項1】 基材の表面が $Y_2O_3$  溶射皮膜によって被覆されていることを特徴とする、プラズマ処理容器内部材。

【請求項2】 トップコートとして形成される $Y_2O_3$  溶射皮膜下に、アンダーコートとして金属皮膜を有することを特徴とする、請求項1に記載のプラズマ処理容器内部材。

【請求項3】 アンダーコートとして形成された金属皮膜と、トップコートとして形成された $Y_2O_3$  溶射皮膜との間に、中間層を有することを特徴とする、請求項2に記載のプラズマ処理容器内部材。

【請求項4】 アンダーコートの金属皮膜は、Niおよびその合金、Wおよびその合金、Moおよびその合金、Tiおよびその合金から選ばれたいずれか1種以上の金属、合金を用いて50~500  $\mu m$ 厚に形成した皮膜であることを特徴とする、請求項2または3に記載のプラズマ処理容器内部材。

【請求項5】 中間層は、 $Al_2O_3$  もしくは $Al_2O_3$  と $Y_2O_3$  との混合皮膜にて形成されていることを特徴とする、請求項3に記載のプラズマ処理容器内部材。

【請求項6】  $Al_2O_3$  と $Y_2O_3$  との混合皮膜からなる中間層は、アンダーコート側では $Al_2O_3$  の濃度が高く、一方トップコート側では $Y_2O_3$  の濃度が高い傾斜濃度をもつ層であることを特徴とする、請求項5に記載のプラズマ処理容器内部材。

【請求項7】  $Y_2O_3$  溶射皮膜は、気孔率が0.5~10%、膜厚50~2000  $\mu m$ の範囲にあることを特徴とする、請求項1~5のいずれか1項に記載のプラズマ処理容器内部材。

【請求項8】 基材の表面に、 $Y_2O_3$  を溶射法にて被覆して、 $Y_2O_3$  溶射皮膜を形成することを特徴とする、プラズマ処理容器内部材の製造方法。

【請求項9】 基材の表面に、CVD法、PVD法あるいは溶射法のいずれか1種以上の表面処理法を適用し、アンダーコートとして、Ni、W、MoもしくはTiおよびそれらの合金からなる金属を被覆し、その上にトップコートとして、 $Y_2O_3$  を被覆することにより複合層を形成することを特徴とする、プラズマ処理容器内部材の製造方法。

【請求項10】 基材の表面に、CVD法、PVD法あるいは溶射法のいずれか1種以上の表面処理法を適用し、Ni、W、MoもしくはTiおよびその合金からなる金属を被覆してアンダーコートを形成し、次いでそのアンダーコートの上に、 $Al_2O_3$  もしくは $Al_2O_3$  と $Y_2O_3$  との混合物を被覆して中間層を形成し、その後その中間層の上に、 $Y_2O_3$  を被覆してトップコートを形成することを特徴とする、プラズマ処理容器内部材の製造方法。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、耐プラズマエロージョン性に優れるプラズマ処理容器内部材とその製造方法に関するものである。とくに本発明は、ハロゲン元素を含む処理ガスのプラズマ雰囲気における、プラズマ処理で使用される、例えば、デポシールド、バッフルプレート、フォーカスリング、インシュレータリング、シールドリング、ベローズカバー、電極などに適用できる技術についての提案である。なお、本発明はまた、単に半導体製造装置の分野のみに限られるものではなく、例えば、液晶デバイスなどのプラズマ処理容器内部品に対しても適用が可能である。以下、主に半導体製造装置の例で説明する。

【0002】

【従来の技術】一般に、半導体および液晶デバイスなどの製造プロセスでは、処理容器内で $BF_3$  や $NF_3$  のようなふっ化物、 $BCl_3$  や $SnCl_4$  などの塩化物、 $HBr$  の如き臭化物をはじめとする処理ガスを使用するため、処理容器内部材が著しく腐食損耗するという問題があった。

【0003】例えば、半導体製造装置のプラズマ処理容器内に使われている材料としては、AlおよびAl合金などの金属材料、その表面に被覆したAlの陽極酸化膜、あるいはボロンカーバイドなどの溶射皮膜、 $Al_2O_3$  や $Si_3N_4$  などの焼結体皮膜、さらにはふっ素樹脂やエポキシ樹脂などの高分子皮膜が知られている。これらの材料は、腐食性の強いハロゲンイオンに接すると、化学的損傷を受けたり、 $SiO_2$ 、 $Si_3N_4$  などの微粒子、およびプラズマによって励起されたイオンによってエロージョン損傷を受けることが知られている。

【0004】とくに、ハロゲン化合物を用いるプロセスでは、反応のより一層の活性化を図るため、しばしばプラズマが用いられる。しかし、このようなプラズマ使用環境下では、ハロゲン化合物は解離して非常に腐食性の強い原子状のF、Cl、Br、Iなどを発生すると同時に、その環境中に $SiO_2$  や $Si_3N_4$ 、Si、Wなどの微粉末状固体物が存在すると、プラズマ処理容器内に用いられている部材が化学的腐食とともに、微粒子によるエロージョン損傷の両方の作用を強く受けることになる。しかも、プラズマが励起された環境は、Arガスのように腐食性のない気体でもイオン化し、これが固体面に強く衝突する現象（イオンボンバードメント）が発生するので、上記容器内に配設されている各種部材はより一層強い損傷を受けることも知られている。

【0005】

【発明が解決しようとする課題】上述した半導体製造装置のように、化学的腐食やエロージョン損傷の激しい分野で用いられる下記の従来部材については、次のような問題点があった。

(1) AlおよびAl合金を陽極酸化して耐食性を有する $Al_2O_3$  膜（アルマイト）を生成させた材料については、ハ

ロゲンガスを含む雰囲気中でプラズマエロージョンを受けると寿命が短いという問題がある。また、Alを含む皮膜なので、 $AlF_3$  のパーティクルが発生し、製造する半導体の製品不良を招く。

(2) 部材表面に、PVD法やCVD法によって、Sc、Y、La、Ce、Yb、Eu、Dyなどの周期律表第3a族元素の酸化物、炭化物、窒化物、ふっ化物などの緻密な皮膜を形成したり、 $Y_2O_3$  の単結晶を適用する技術がある(特開平10-4083号公報)。しかし、この技術は、成膜速度が遅く生産性に劣るほか、複数の皮膜部材を同時に形成(複合皮膜)できないという欠点がある。

【0006】そこで、本発明の目的は、ハロゲンガスが含まれるような環境による化学的腐食による損傷ならびにプラズマエロージョンによる損傷に対する抵抗力の大きいプラズマ処理容器等に供される表面処理部材と、その有利な製造方法とを提案するところにある。

【0007】

【課題を解決するための手段】本発明は、従来技術が抱えている上述した問題ならびに欠点を、以下に要約して述べる解決手段の採用によって克服したものである。すなわち、本発明の構成を整理すると、次の通りである。

【0008】(1) 基材の表面に、溶射法によって気孔率0.2~10%、厚さ50~2000 $\mu m$ の $Y_2O_3$  溶射皮膜のみからなる層を形成した被覆部材であること。

【0009】(2) 環境の腐食性が強い場合、例えば、ハロゲン化合物を含む雰囲気中におけるプラズマ発生条件下の場合には、基材の表面に、アンダーコートとして、好ましくは溶射法により、 $Y_2O_3$  溶射皮膜との密着性に優れた、Niおよびその合金、Wおよびその合金、Moおよびその合金、Tiおよびその合金の中から選ばれる1種以上の金属・合金の皮膜を、50~500 $\mu m$ の厚さに被覆し、そしてそのアンダーコートの上に、 $Y_2O_3$  溶射皮膜を50~2000 $\mu m$ 厚さに加工して複合層を形成した被覆部材であること。

【0010】(3) 基材の表面に、金属皮膜(好ましくは溶射皮膜)をアンダーコートとして施工した後、そのアンダーコートの上に、中間層として $Al_2O_3$  の皮膜(好ましくは溶射皮膜)を形成し、さらにその中間層の上に、トップコートとして溶射によって $Y_2O_3$  溶射皮膜を形成してなる多層状複合層を形成した被覆部材であること。

【0011】(4) 基材の表面に、金属皮膜(好ましくは溶射皮膜)をアンダーコートとして施工した後、そのアンダーコートの上に、中間層として $Al_2O_3$  と $Y_2O_3$  の混合物の皮膜(好ましくは溶射皮膜)を形成し、さらにその中間層の上に、トップコートとして溶射法によって $Y_2O_3$  溶射皮膜を形成した多層状複合層を形成した被覆部材であること。

【0012】(5) 基材の表面に、直接またはアンダーコートや中間層を施工した上に形成する $Y_2O_3$  溶射皮膜

は、純度95%以上の $Y_2O_3$  粉末を使用し、この粉末を大気中でプラズマ溶射するか、実質的に酸素を含まないArガスの減圧雰囲気下でプラズマ溶射するか、あるいは高速フレイム溶射法や爆発溶射法などから選ばれた溶射方法を適用して得られる溶射皮膜を被覆した部材であること。なかでも、Arガスの減圧プラズマ溶射による方法が、耐食性の改善にも有効である。

【0013】

【発明の実施の形態】発明者らの研究によると、従来技術が抱えている上述した課題について鋭意研究した結果、プラズマ処理容器内部材の損傷は、ハロゲンガスによる化学的腐食による損傷と、プラズマエロージョンによる損傷とが考えられる。特に、この部材がプラズマによって励起されたハロゲンを含む雰囲気中で使用される場合、耐プラズマエロージョン性を起因とする損傷を防ぐことこそが重要であり、そうすれば化学的腐食防止に対しても有効に作用するとの知見を得た。そこで、本発明では主として、耐プラズマエロージョン性に対して有効な皮膜の形成について研究した。その結果として、上掲の本発明にかかる部材を開発した。

【0014】すなわち、その課題解決の手段として採用した本発明は、基本的には、金属、セラミックス、炭素材料などの基材表面に、溶射法によって、 $Y_2O_3$  のみからなる溶射皮膜を形成することにした。そして、こうした部材が使用される環境の腐食性が強い場合には、前記 $Y_2O_3$  溶射皮膜の下に、耐ハロゲンガス腐食性の強い特性を示す金属のアンダーコートを設けると共に、さらには $Al_2O_3$  や $Y_2O_3$  の中間層をも設けて複合化させる方法である。以下、かかる本発明部材の構成について詳しく説明する。

【0015】(1) 基材について

上記溶射皮膜の施工対象となる基材としては、ステンレス鋼を含む各種の鋼、アルミニウムおよびアルミニウム合金、タングステンおよびタングステン合金、チタンおよびチタン合金、モリブデンおよびモリブデン合金および炭素ならびに酸化物系、非酸化物系セラミックス焼結体、あるいは炭素質材料などが好適である。なお、銅および銅合金は、プラズマエロージョンやハロゲン化合物による腐食作用によって放出され、環境汚染の原因となるので好ましくない。従って、もし装置の構成上、銅および銅合金の使用が必要な場合は、電気めっき、化学めっき、蒸着などの手段でCr、Niなどで被覆しておく必要がある。

【0016】(2) 皮膜構成について

上記基材表面への皮膜の形成は、基材をプラスト処理した後、 $Y_2O_3$  を直接に溶射して成膜するか、または、基材表面にまずアンダーコート層として、耐ハロゲンガス腐食性の強い金属材料からなる皮膜を、PVD処理、CVD処理もしくは溶射処理して形成し、そのアンダーコートの上に $Y_2O_3$  粉末をトップコートとして溶射して複

合層とする方法が好ましい。この場合において、前記金属アンダーコート（溶射皮膜等）は、膜厚は50～500  $\mu$ mの範囲内とする。アンダーコート層が50  $\mu$ mより薄いとアンダーコートとしての作用効果が弱く、一方、500  $\mu$ mを超える厚さでは効果が飽和するので肥厚化の意味がなく、得策でないからである。かかるアンダーコート用金属材料としては、ニッケルおよびニッケル合金、タングステンおよびタングステン合金、モリブデンおよびモリブデン合金、チタンおよびチタン合金などが好適である。

【0017】一方、トップコートとなる $Y_2O_3$ 溶射皮膜は、基材表面に直接施工したものであれ、また、前記アンダーコートの上に溶射して複合層にしたものであれ、さらには中間層として $Al_2O_3$ や $Al_2O_3 + Y_2O_3$ 皮膜を設けた場合であれ、いずれにしても50～2000  $\mu$ mの厚さに施工することが好ましい。その理由は、50  $\mu$ mより薄い層ではプラズマエロージョンによる損傷の防止に対して効果が乏しく、一方、2000  $\mu$ mより厚くしても効果が飽和して経済的でないからである。

【0018】なお、トップコートの $Y_2O_3$ 溶射皮膜の気孔率は、0.5～10%の範囲がよい。0.5%以下の皮膜は溶射法では製造が困難であり、また、10%以上の気孔率の皮膜では耐食性、耐プラズマエロージョン性に劣るからである。

【0019】(3) 部材最表面層の $Y_2O_3$ 溶射皮膜について

本発明の最も特徴とする構成は、基材の最表面層を、ハロゲンガスを含む雰囲気中で耐プラズマエロージョン性を示す材料として $Y_2O_3$ を採用し、これを溶射層として被覆形成するところにある。即ち、本発明の研究によると、 $Y_2O_3$ は、比重が4.84、融点が2410℃で、酸素との化学的結合力が強いので、ハロゲンガスを含む雰囲気中でプラズマエロージョン作用を受けても、安定した状態を維持することがわかった。ただし、この $Y_2O_3$ 純度は95%以上のものを用いることが必要であり、Fe、Mg、Cr、Al、Ni、Siなどの不純物が酸化物として含まれていると、耐エロージョン性が低下するので好ましくない。98%以上の純度のものがより好ましい。なお、この $Y_2O_3$ 溶射皮膜の直下に形成させる中間層の $Al_2O_3$ は、化学的に安定であるうえ、大気プラズマ溶射や減圧プラズマ溶射環境下においても変化が少なく、 $Y_2O_3$ の耐プラズマエロージョン性を補償する作用を担うものである。

【0020】(4) 被覆方法

a. 溶射皮膜の形成

本発明においては、少なくとも最表面層トップコートの $Y_2O_3$ 皮膜は溶射皮膜とする。そして、好ましくはこのトップコート溶射皮膜下にはこの皮膜をさらに強化する意味で、全体の皮膜構成を次のような多層構造にすることが好ましい。即ち、基材の表面に、金属溶射皮膜のアンダーコートを施工した後、その上に $Al_2O_3$ 溶射皮膜

もしくは傾斜配合にかかる $Al_2O_3$ と $Y_2O_3$ との混合物溶射皮膜を中間層として施工し、さらに、その上にトップコートとして、 $Y_2O_3$ 溶射皮膜を形成するものである。このような皮膜構成が好ましい理由は、金属溶射皮膜に比較して耐食性、耐プラズマエロージョン性に優れる $Al_2O_3$ を中間層として形成することで、溶射皮膜を多層構造化し、皮膜の貫通気孔を少なくして耐食性、耐エロージョン性を向上させることができるからである。しかも、中間層としての $Al_2O_3$ は、アンダーコートおよびトップコートの両方とも良好な密着性を発揮する。この意味において、中間層は、 $Al_2O_3$ と $Y_2O_3$ との混合物の層とすることがより好ましく、この場合、アンダーコート側の $Al_2O_3$ 濃度を高くする一方、トップコート側では $Y_2O_3$ 濃度が高くなるような傾斜配合にかかる混合層とすることが好ましい。このような中間層の形成は、溶射法を採用すると容易に施工することができるので、中間層が溶射皮膜として形成されることは好ましい実施形態といえる。なお、中間層の厚さは、トップコートの $Y_2O_3$ 溶射皮膜と同一の範囲が好適である。

【0021】本発明において、金属や $Al_2O_3$ 、 $Y_2O_3$ の溶射皮膜を形成するには、大気プラズマ溶射法または、実質的に酸素を含まない雰囲気中でのプラズマ溶射法が好適であるが、高速フラーム溶射や爆発溶射法による施工も可能である。

【0022】b. CVD法およびPVD法によるアンダーコート、中間層の形成

CVD法では、所要の金属ハロゲン化合物の蒸気を、水素などによって還元析出させ、その後酸素または酸素化合物によって酸化させるが、大気中で加熱することによって、酸化物皮膜に変化させることによって成膜する。一方、PVD法では、焼結体または粉末を原料とし、これに電子ビームを照射して揮散させ、これを基材表面に析出させることによって成膜する。一般に、CVD法、PVD法による皮膜の形成は、薄膜（例えば50  $\mu$ m前後）の施工に適している。

【0023】(5) 本発明にかかる部材の使用環境について

本発明にかかる部材表面に被覆した $Y_2O_3$ 溶射皮膜は、ハロゲン化合物を含む雰囲気下において発生するプラズマ環境下で使用する場合に特に有用である。

【0024】もちろん、ハロゲン元素またはハロゲン化合物を含まない $N_2$ 、 $H_2$ などの雰囲気下におけるプラズマエロージョン作用に対しても本発明は有効であり、この場合はとくにハロゲンを含む雰囲気と比較して、エロージョン損傷が緩やかであるので、本発明にかかる皮膜被覆部材は長期間にわたって安定した性能を発揮する。

【0025】

【実施例】実施例1

この実施例では、アルミニウム製試験片（寸法：幅50mm

×長50mm×厚5mm)の片面をブラスト処理によって粗面化した後、 $Y_2O_3$ 溶射材料を用いて大気プラズマ溶射法と、Arガスで雰囲気圧力を50～200 hPaに制御した減圧プラズマ溶射法によって、それぞれ膜厚300  $\mu m$ の $Y_2O_3$ 溶射皮膜を形成した。また、アルミニウム製試験片の片面に、大気プラズマ溶射法によって、Ni-20%Al合金のアンダーコート、膜厚100  $\mu m$ 厚に施工したあと、前記 $Y_2O_3$ をトップコートとして300  $\mu m$ 厚に被覆したものを作製した。その後、これらの試験片表面に形成されている $Y_2O_3$ 溶射皮膜の気孔率、密着強さ、および熱衝撃試験(500℃に維持されている電気炉中で20分加熱した後、炉外にて空冷の操作を1サイクルとして10サイクル繰り返し試験)を行った。なお、比較例として、Al \*

\* $Y_2O_3$ の溶射皮膜についても同じ条件、同じ工程で施工したものを供試した。

【0026】表1は、このときの試験結果をまとめたものである。本発明に適合する皮膜は、試験片の表面に $Y_2O_3$ 皮膜を直接被覆したもの(No.1、3)をはじめ、アンダーコートを施した上に $Y_2O_3$ 皮膜を形成したもの(No.2、4)を含む全ての皮膜が良好な密着性と耐熱衝撃性を示し、 $Al_2O_3$ 皮膜に比較しても全く遜色がない。とくに、減圧プラズマ溶射法で形成された $Y_2O_3$ 皮膜は、大気溶射法の皮膜に比較して気孔率が少ないので、良好な耐食性も期待できる。

【0027】

【表1】

No	溶射法	皮膜の構成		気孔率 (%)	密着強さ (MPa)	熱衝撃試験 外観目視	備考
		アンダーコート	トップコート				
1	大気 プラズマ	なし	$Y_2O_3$	5～9	35～38	剥離なし	実施例
2		Ni-20Al	$Y_2O_3$	6～8	38～41	剥離なし	
3	減圧 プラズマ	なし	$Y_2O_3$	0.2～3	40～41	剥離なし	
4		Ni-20Al	$Y_2O_3$	0.3～4	40～44	剥離なし	
5	大気 プラズマ	なし	$Al_2O_3$	8～12	38～42	剥離なし	比較例
6		Ni-20Al	$Al_2O_3$	9～12	35～44	剥離なし	
7	減圧 プラズマ	なし	$Al_2O_3$	0.5～5	38～44	剥離なし	
8		Ni-20Al	$Al_2O_3$	0.6～7	39～43	剥離なし	

(備考)

(1) 皮膜厚さ：アンダーコート 100 $\mu m$ 、トップコート 300 $\mu m$

(2) 密着強さは JIS H8666セラミック溶射皮膜試験方法規定の密着強さ試験法による。

(3) 熱衝撃試験：500℃×20min→室温(空冷) 繰り返し10回後の外観観察

## 【0028】実施例2

この実施例では、50mm×100mm×5mm厚のアルミニウム製基材を用いて、表2に示すような表面処理を施した後、それぞれの基材から寸法20mm×20mm×5mmの試験片を切り出し、さらに表面処理面が10mm×10mmの範囲が露出するように他の部分をマスクし、下記条件にて20時間照射して、プラズマエロージョンによる損傷量を減肉厚さとして求めた。

### (1) ガス雰囲気と流量条件

$CF_4$ 、Ar、 $O_2$ の混合ガスを下記条件の雰囲気とした。

$CF_4$ /Ar/ $O_2$  = 100/1000/10 (1分間当たりの流量 $cm^3$ )

### (2) プラズマ照射出力

高周波電力 : 1300 W

圧力 : 133.3 Pa

【0029】その試験結果を表2に示した。この表2に示す結果から明らかなように、比較例の現行技術による陽極酸化皮膜(No.8)をはじめ、 $B_4C$ 溶射皮膜(No.10)は、いずれもプラズマエロージョンによる損傷量が大きく、実用的でないことがうかがえる。ただ、比較例においても $Al_2O_3$ 溶射皮膜(No.9)は比較的良好な耐プラズマエロージョン性を示した。これに対し、本発明の $Y_2O_3$ 溶射皮膜は、極めて優れた耐プラズマエロージョン性を発揮し、ハロゲン化合物を含む雰囲気下においても良好な性能を維持することが認められた。

【0030】

【表2】

No	溶射法	表面処理法	アンダーコートの有無	エロージョン損失深さ(μm)	備考
1	Y <sub>2</sub> O <sub>3</sub> (99.9%)	溶射	有	6.2	実施例
2			無	6.1	
3	Y <sub>2</sub> O <sub>3</sub> (99.8%)	溶射	有	7.6	
4			無	7.2	
5	Y <sub>2</sub> O <sub>3</sub> (99.5%)	溶射	有	6.5	
6			無	6.3	
7	Y <sub>2</sub> O <sub>3</sub> (99.9%)	PVD	無	6.6	比較例
8	Al <sub>2</sub> O <sub>3</sub>	陽極酸化	無	39.5	
9	Al <sub>2</sub> O <sub>3</sub>	溶射	有	8.1	
10	B <sub>4</sub> C	溶射	有	28.0	
11	石英	—	無	39.0	

(備考)

- (1) 溶射は大気プラズマ溶射法を用い、アンダーコートの膜厚80μm  
Y<sub>2</sub>O<sub>3</sub>、Al<sub>2</sub>O<sub>3</sub>などのトップコートの膜厚は200μmに成膜  
(2) アンダーコートの材質は80%Ni-20%Al  
(3) 陽極酸化はJIS H8601規定のAA25に準じて成膜させたものである。

## 【0031】実施例3

この実施例では、幅50mm×長さ100mm×厚5mmのアルミニウム製基材上に、アンダーコートとして80%Ni-20%Alを80μm、中間層としてAl<sub>2</sub>O<sub>3</sub>、またはAl<sub>2</sub>O<sub>3</sub> 50vol%/Y<sub>2</sub>O<sub>3</sub> 50vol%の混合物を100μm、その上にY<sub>2</sub>O<sub>3</sub>を200μm厚に、それぞれ大気プラズマ溶射法によって成膜した後、実施例2の条件でプラズマエロージョン試験を実施した。その結果、本発明の溶射皮膜は、最表層部(トップコート)にY<sub>2</sub>O<sub>3</sub>溶射皮膜を形成している限り、中間層としてAl<sub>2</sub>O<sub>3</sub>、Al<sub>2</sub>O<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub>混合物層を配設しても、耐プラズマエロージョン性には影響を受けず、20時間の照射で6.1~7.5μmの消失が認められたに過ぎず、多層構造皮膜でも十分な性能を発揮することが認められた。

## 【0032】実施例4

この実施例では、現行のアルミニウム製基材を陽極酸化(アルマイト処理)した試験片と、基材上にアンダーコートとして80%Ni-20%Alの合金皮膜を100μm厚に被覆し、その上にトップコートとしてY<sub>2</sub>O<sub>3</sub>皮膜を250μm、それぞれプラズマ溶射法によって形成した試験片を用いて、下記条件でプラズマエッチングを行い、エッチングによって削られて飛散するパーティクル粒子の数は同じチャンパー内に静置した直径8インチのシリコンウエハーの表面に付着する粒子数によって比較した。な

お、付着する粒子数は表面検査装置によって調査し、概ね粒径0.2μm以上の粒子を対象にして行った。

## (1) ガス雰囲気と流量条件

CHF<sub>3</sub>、O<sub>2</sub>、Arをそれぞれ下記のような混合比で流通した。

CHF<sub>3</sub>/O<sub>2</sub>/Ar=80/100/160(1分間当たりの流量cm<sup>3</sup>)

## (2) プラズマ照射出力

高周波電力 : 1300 W

圧力 : 4 Pa

温度 : 60 °C

【0033】この実験の結果、陽極酸化(アルマイト膜)した試験片では、プラズマ照射17.5時間後、一般的なチャンパー内のパーティクル管理値の30個を超え25時間後では150個以上となった。このパーティクルの組成は、Al、Fからなるものであった。これに対し、本発明に適合するY<sub>2</sub>O<sub>3</sub>溶射皮膜では、70時間照射後になって、やっと管理限界値を超える程度にとどまり、優れた耐プラズマエロージョン性を示した。

## 【0034】

【発明の効果】以上説明したように本発明によれば、金属質、または非金属質基材の上に、Y<sub>2</sub>O<sub>3</sub>溶射皮膜を直接形成するか、金属質のアンダーコートを施工した上に、Y<sub>2</sub>O<sub>3</sub>溶射皮膜を形成した部材では、ハロゲン化合

物を含むガス雰囲気下におけるプラズマエロージョン作用を受ける環境下で使用した場合に、優れた抵抗性を示す。このため、長時間にわたってプラズマエッチング作業を続けても、チャンバー内はパーティクルによる汚染が少なく、高品質製品を効率よく生産することが可能と\*

\*なる。また、チャンバー内のパーティクルによる汚染速度が遅くなるため、清浄化作業の間隔が長くなり、生産性の向上が期待でき、プラズマ処理容器内部材として極めて有効である。

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MIHASHI YASUSHI**(54) MEMBER INSIDE PLASMA TREATMENT CHAMBER, AND MANUFACTURING METHOD THEREFOR**

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a member inside a plasma treatment chamber, excellent in plasma erosion resistance, and to provide an advantageous manufacturing method therefor.

**SOLUTION:** The surface of a base material is coated with a multilayered combined layer consisting of a metal film formed as an undercoat, an Al<sub>2</sub>O<sub>3</sub> film formed as an intermediate layer on the undercoat, and a Y<sub>2</sub>O<sub>3</sub> sprayed deposit formed as a topcoat on the intermediate layer.

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CLAIMS

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## [Claim(s)]

[Claim 1] Interior material of a plasma treatment container characterized by covering the front face of a base material with 2OY3 sprayed coating.

[Claim 2] Interior material of a plasma treatment container according to claim 1 characterized by having a metallic film as an under coat under the Y2O3 sprayed coating formed as topcoat.

[Claim 3] Interior material of a plasma treatment container according to claim 2 characterized by having an interlayer between the metallic film formed as an under coat, and 2OY3 sprayed coating formed as topcoat.

[Claim 4] The gap or one or more sorts of metals which be chosen from nickel and its alloy, W and its alloy, Mo and its alloy, Ti, and its alloy, and an alloy are used for the metallic film of an under coat, and it is 50-500. Interior material of a plasma treatment container according to claim 2 or 3 characterized by being the coat formed in mum thickness.

[Claim 5] an interlayer and aluminum 2O3 -- or -- Interior material of a plasma treatment container according to claim 3 characterized by being formed in the mixed coat with aluminum 2O3 andY2O3.

[Claim 6] The interlayer who consists of a mixed coat with aluminum 2O3 andY2O3 is at an under coat side. Interior material of a plasma treatment container according to claim 5 characterized by being the layer in which the concentration of aluminum 2O3 is high, and, on the other hand, has inclination concentration with the high concentration of Y2O3 by the topcoat side.

[Claim 7] 2OY3 sprayed coating is the interior material of a plasma treatment container given in any 1 term of claims 1-5 characterized by porosity being in the range which is 50-2000 micrometers of thickness 0.5 to 10%.

[Claim 8] The manufacture approach of the interior material of a plasma treatment container which covers Y2O3 with a spraying process and is characterized by forming 2OY3 sprayed coating on the surface of a base material.

[Claim 9] The manufacture approach of the interior material of a plasma treatment container which applies any one or more sorts of surface treatment methods of a CVD method, PVD, or a spraying process, covers the metal which consists of nickel, W, Mo or Ti, and those alloys as an under coat on the surface of a base material, and is characterized by forming a compound layer by covering Y2O3 as topcoat on it.

[Claim 10] On the surface of a base material, any one or more sorts of surface treatment methods of a CVD method, PVD, or a spraying process are applied. Cover the metal which consists of nickel, W, Mo or Ti, and its alloy, and an under coat is formed. subsequently, the under coat top -- aluminum 2O3 -- or -- The manufacture approach of the interior material of a plasma treatment container characterized by covering mixture with aluminum 2O3 andY2O3, forming an interlayer, covering Y2O3 and forming topcoat on the interlayer after that.

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[Translation done.]

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the interior material of a plasma treatment container which is excellent in plasma-proof erosion nature, and its manufacture approach. Especially this invention is a proposal about the technique which it is used, for example, can be applied to DEPOSHIRUDO, a baffle plate, a focal ring, an insulator ring, a shielding ring, bellows covering, an electrode, etc. by plasma treatment in the plasma ambient atmosphere of the raw gas containing a halogen. In addition, this invention is not restricted only to the field of semiconductor fabrication machines and equipment, and can be applied also to plasma treatment container internals, such as a liquid crystal device, again. Hereafter, the example of semiconductor fabrication machines and equipment mainly explains.

[0002]

[Description of the Prior Art] general -- manufacture processes, such as a semi-conductor and a liquid crystal device, -- the inside of a processing container -- a \*\*\*\* ghost like BF<sub>3</sub> or NF<sub>3</sub>, and BCl<sub>3</sub> Chlorides, such as SnCl<sub>4</sub>, and HBr like -- in order to use raw gas including a bromide, there was a problem that the interior material of a processing container carried out corrosion consumption remarkably.

[0003] for example, sprayed coatings, such as an anodized film of aluminum covered on metallic materials, such as aluminum and aluminum alloy, and the front face of those as an ingredient currently used in the plasma treatment container of semiconductor fabrication machines and equipment, or boron carbide, and aluminum 2O<sub>3</sub> sintered compact coats, such as Si<sub>3</sub>N<sub>4</sub>, -- macromolecule coats, such as a fluororesin and an epoxy resin, are known further. If these ingredients touch strong corrosive halogen ion, chemical injury is received or receiving erosion damage with particles, such as SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>, and the ion excited by the plasma is known.

[0004] Especially, in the process using a halogenated compound, in order to attain much more activation of a reaction, the plasma is often used. however -- at the same time it dissociates a halogenated compound and it generates F, Cl, corrosive Br, corrosive I, etc. of the shape of a strong atom very much under such a plasma operating environment -- the inside of the environment -- SiO<sub>2</sub> When impalpable powder-like solids, such as Si<sub>3</sub>N<sub>4</sub>, and Si, W, exist, the member used into the plasma treatment container will receive strongly an operation of erosion damages on both by the particle with chemical corrosion. And the environment where the plasma was excited is the phenomenon in which also ionize the gas which does not have corrosive like Ar gas, and this collides to a solid-state side strongly. (ion bombardment) Since it generates, it is also known that the various members currently arranged in the above-mentioned container will receive still stronger damage.

[0005]

[Problem(s) to be Solved by the Invention] Like the semiconductor fabrication machines and equipment mentioned above, there were the following troubles about the following conventional member used in the intense field of chemical corrosion or erosion damage.

(1) aluminum and aluminum alloy are anodized and it has corrosion resistance. 2Oaluminum<sub>3</sub> film (alumite) About the ingredient made to generate, when plasma erosion is received in the ambient atmosphere containing halogen gas, there is a problem that a life is short. Moreover, since it is a coat containing aluminum, the particle of AlF<sub>3</sub> occurs and invites the poor product of the semi-conductor to manufacture.

(2) a member front face -- PVD and a CVD method -- the [, such as Sc, Y, La, Ce, Yb, Eu, and Dy, / periodic table ] -- precise coats, such as an oxide of 3a group element, carbide, a nitride, and a \*\*\*\* ghost, are formed, or there is a technique which applies the single crystal of Y<sub>2</sub>O<sub>3</sub> (JP,10-4083,A) . However, a membrane formation rate is late inferior to productivity, and also this technique forms two or more coat members in coincidence. (compound coat) There is a fault that it cannot do.

[0006] Then, the purpose of this invention is in the place which proposes the surface treatment member with which the large plasma treatment container of drag force to the damage by the chemical corrosion by environment in which halogen gas is contained, and damage by plasma erosion etc. is presented, and its advantageous manufacture approach.

[0007]

[Means for Solving the Problem] This invention is conquered by adoption of a solution means to summarize and describe below the problem and fault which the conventional technique is holding and which were

mentioned above. That is, it is as follows when the configuration of this invention is arranged.

[0008] (1) It is the covering member in which the layer which consists only of 2OY3 sprayed coating with a% [ of porosity ] of 0.2 - 10 and a thickness of 50-2000 micrometers by the spraying process was formed on the surface of the base material.

[0009] (2) When corrosive [ environmental ] is strong, in under the plasma generating conditions in the ambient atmosphere containing a halogenated compound On the surface of the base material, excelled in adhesion with 2OY3 sprayed coating by the spraying process preferably as an under coat. The coat of one or more sorts of the metal and alloys chosen from nickel and its alloy, W and its alloy, Mo and its alloy, Ti, and its alloy 50-500 It is the covering member which covered in the thickness of mum, and processed 2OY3 sprayed coating into 50-2000-micrometer thickness on the under coat, and formed the compound layer.

[0010] (3) To the front face of a base material, it is a metallic film. (preferably sprayed coating) It is an interlayer on the under coat after constructing as an under coat. Coat of aluminum 2O3 (preferably sprayed coating) It is the covering member which formed and formed further the multilayer-like compound layer which comes to form 2OY3 sprayed coating by thermal spraying as topcoat on the interlayer.

[0011] (4) To the front face of a base material, it is a metallic film. (preferably sprayed coating) It is an interlayer on the under coat after constructing as an under coat. Coat of the mixture of aluminum 2O3 and Y2O3 (preferably sprayed coating) It is the covering member which formed and formed further the multilayer-like compound layer which formed 2OY3 sprayed coating by the spraying process as topcoat on the interlayer.

[0012] (5) 2OY3 sprayed coating which constructed direct or the under coat, and the interlayer and is formed upwards on the surface of a base material [ whether the plasma metal spray of this powder is carried out in atmospheric air by using 2OY3 powder of 95% or more of purity, and ] It is the member which covered the sprayed coating obtained with the application of the thermal-spraying approach which carried out the plasma metal spray under the reduced pressure ambient atmosphere of Ar gas which does not contain oxygen substantially, or was chosen from the high-speed flame-spraying method, the detonation-flame-spraying method, etc. Especially, the approach by low pressure plasma spraying of Ar gas is effective also for a corrosion resistance improvement.

[0013]

[Embodiment of the Invention] As a result of inquiring wholeheartedly about the technical problem which the conventional technique is holding and which was mentioned above according to research of artificers, the damage on the interior material of a plasma treatment container can consider damage by the chemical corrosion by halogen gas, and damage by plasma erosion. When this member was especially used in the ambient atmosphere containing the halogen excited by the plasma, knowledge that it is important just preventing the damage which considers plasma-proof erosion nature as a reason, then it acts effectively also to chemical corrosion prevention was acquired. So, in this invention, it inquired about formation of an effective coat mainly to plasma-proof erosion nature. As the result, the member concerning this invention of upper \*\* was developed.

[0014] That is, fundamentally, this invention adopted as a means of the technical-problem solution was made to form the sprayed coating which consists only of Y2O3 in base material front faces, such as a metal, ceramics, and a carbon material, by the spraying process. And when corrosive [ of the environment where such a member is used ] is strong, while establishing the under coat of the metal in which a strong halogen-proof gas corrosive property is shown in the bottom of said 2OY3 sprayed coating, it is in a pan. It is the approach of also making the interlayer of aluminum Y2O3 [ 2O3 ] preparing and compound-izing. Hereafter, the configuration of this this invention member is explained in detail.

[0015] (1) As a base material set as the construction object of the above-mentioned sprayed coating about a base material, it is the steel, the aluminum and the aluminium alloy, the tungsten and the tungsten alloy, the titanium and the titanium alloy, the molybdenum, the molybdenum alloy, the carbon, and the oxide system of the various kinds containing stainless steel, A non-oxide system ceramic sintered compact or a carbonaceous ingredient is suitable. In addition, since copper and a copper alloy are emitted by the corrosive action by plasma erosion or the halogenated compound and cause environmental pollution, they are not desirable. Therefore, constitutionally, when [ of equipment ] copper and a copper alloy need to be used, means, such as electroplating, chemical plating, and vacuum evaporation, need to cover with Cr, nickel, etc.

[0016] (2) [ whether about a coat configuration, after formation of a coat on the above-mentioned base

material front face carries out blasting processing of the base material, it carries out thermal spraying of Y<sub>2</sub>O<sub>3</sub> directly, and forms membranes, and ] Or the approach of PVD processing, CVD-processing or thermal-spraying processing, and forming in a base material front face the coat which consists of a strong halogen-proof gas corrosive metallic material as an under coat layer first, and using 2OY<sub>3</sub> powder as topcoat, it carrying out thermal spraying on the under coat, and using as a compound layer is desirable. In this case, said metal under coat s (sprayed coating etc.) Thickness is 50-500. It considers as within the limits of mum. When an under coat layer is thinner than 50 micrometers, the operation effectiveness as an under coat is weak, and on the other hand, it is 500. Since effectiveness is saturated with the thickness exceeding mum, there is no semantics of the tylosis, and it is because it is not a best policy. As this metallic material for under coats, nickel and a nickel alloy, a tungsten and a tungsten alloy, molybdenum and a molybdenum alloy, titanium, a titanium alloy, etc. are suitable.

[0017] on the other hand, construct 2OY<sub>3</sub> sprayed coating used as topcoat directly on a base material front face -- moreover, carry out thermal spraying on said under coat, and make it a compound layer -- further -- as an interlayer aluminum 2O<sub>3</sub> the case where 2Oaluminum2O<sub>3</sub>+Y<sub>3</sub> coat is prepared -- be -- it is desirable to construct in thickness of 50-2000 micrometers anyway. The reason is that effectiveness saturates and is not more economical than 50 micrometers in a film even if effectiveness is scarce and makes it thicker than 2000 micrometers on the other hand to prevention of damage by plasma erosion.

[0018] In addition, the porosity of 2OY<sub>3</sub> sprayed coating of topcoat has 0.5 - 10% of good range. 0.5 In a spraying process, the coat below % is difficult to manufacture, and is because it is inferior to corrosion resistance and plasma-proof erosion nature in the coat of 10% or more of porosity.

[0019] (3) About 2OY<sub>3</sub> sprayed coating of a member maximum surface layer, the configuration of this invention by which it is characterized most adopts Y<sub>2</sub>O<sub>3</sub> as an ingredient in which plasma-proof erosion nature is shown in the ambient atmosphere which contains halogen gas for the maximum surface of a base material, and is in the place which carries out covering formation by making this into a thermal-spraying layer. Namely, as for Y<sub>2</sub>O<sub>3</sub>, according to research of this invention, it turned out that it maintains the condition of having been stabilized even if specific gravity receives a plasma erosion operation in the ambient atmosphere in which it is 2410 degrees C, and 4.84 and the melting point contain halogen gas since chemical bonding strength with oxygen is strong. However, this 2OY<sub>3</sub> purity needs to use 95% or more of thing, and if impurities, such as Fe, Mg, Cr, aluminum, nickel, and Si, are contained as oxide, since erosion-proof nature will fall, it is not desirable. The thing of 98% or more of purity is more desirable. In addition, interlayer who makes it form directly under this 2OY<sub>3</sub> sprayed coating A chemically stable top, as for aluminum 2O<sub>3</sub>, there is little change under an atmospheric-air plasma metal spray or a low-pressure-plasma-spraying environment, and it bears the operation which compensates the plasma-proof erosion nature of Y<sub>2</sub>O<sub>3</sub>.

[0020] (4) Let 2OY<sub>3</sub> coat of the maximum surface topcoat at least be a sprayed coating in formation this invention of a covering approach a. sprayed coating. And it is the semantics which strengthens this coat further under this topcoat sprayed coating preferably, and it is desirable to make the whole coat configuration into the following multilayer structure. That is, after constructing the under coat of a metallizing coat on the surface of a base material, 2Oaluminum<sub>3</sub> sprayed coating or inclination combination is started on it. A mixture sprayed coating with aluminum 2O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> is constructed as an interlayer, and 2OY<sub>3</sub> sprayed coating is further formed as topcoat on it. The reason nil why such a coat configuration is desirable is excellent in corrosion resistance and plasma-proof erosion nature as compared with a metallizing coat. It is because a sprayed coating can be multilayer-structure-ized, penetration pore of a coat can be lessened and corrosion resistance and erosion-proof nature can be raised by forming aluminum 2O<sub>3</sub> as an interlayer. And it is as an interlayer. Adhesion with both an under coat and topcoat good [ aluminum 2O<sub>3</sub> ] is demonstrated. In this semantics, it is more desirable to consider as an interlayer and the layer of mixture with aluminum 2O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>, and it is an under coat side in this case. While making 2Oaluminum<sub>3</sub> concentration high, in a topcoat side, it is desirable to consider as the mixolimnion concerning inclination combination to which 2OY<sub>3</sub> concentration becomes high. Since such an interlayer's formation can be easily constructed if a spraying process is adopted, it can be called desirable operation gestalt that an interlayer is formed as a sprayed coating. In addition, the same range as 2OY<sub>3</sub> sprayed coating of topcoat is suitable for an interlayer's thickness.

[0021] It sets to this invention and is a metal. Although an atmospheric-air plasma metal spray method or the plasma metal spray method in the inside of the ambient atmosphere which does not contain oxygen

substantially is suitable in order to form aluminum  $2O_3$  and the sprayed coating of  $Y_2O_3$ , construction by high-speed flame spraying or the detonation-flame-spraying method is also possible.

[0022] b. Under coat by the CVD method and PVD, Although a reduction deposit is carried out by hydrogen etc. and the steam of a necessary metal halogenated compound is oxidized with oxygen or an oxygen compound after that in an interlayer's formation CVD method, membranes are formed by making it change to an oxide film by heating in atmospheric air. On the other hand, in PVD, a sintered compact or powder is used as a raw material, in this, an electron beam is irradiated, and is vaporized, and membranes are formed by depositing this on a base material front face. Formation of the coat generally according to a CVD method and PVD is a thin film. (for example, before or after 50 micrometers) It is suitable for construction.

[0023] (5)  $2OY_3$  sprayed coating covered on the member front face which starts this invention about the operating environment of the member concerning this invention is useful especially when using it under the plasma environment generated under the ambient atmosphere containing a halogenated compound.

[0024] Of course, since erosion damage is loose as compared with the ambient atmosphere which is effective as for this invention and contains a halogen especially in this case also to the plasma erosion operation under ambient atmospheres, such as  $N_2$  which does not contain a halogen or a halogenated compound, and  $H_2$ , the coat covering member concerning this invention demonstrates the engine performance stabilized over the long period of time.

[0025]

[Example] an example 1 -- this example -- test piece made from aluminum (dimension: 5mm of 50mm x thickness of width-of-face [ of 50mm ] x length)  $2OY$  after carrying out surface roughening of one side by blasting processing<sup>3</sup> thermal spray material -- using -- an atmospheric-air plasma metal spray method and Ar gas -- the ambient pressure force -- 50 - 200 hPa the controlled low-pressure-plasma-spraying method -- respectively -- thickness 300 m $Y_2O_3$  sprayed coating was formed. Moreover, it is thickness 100 about the under coat of a nickel-20%aluminum alloy by the atmospheric-air plasma metal spray method to one side of the test piece made from aluminum. It is 300, using said  $Y_2O_3$  as topcoat, after constructing to mum thickness. What was covered to mum thickness was produced. Then, the porosity of  $2OY_3$  sprayed coating currently formed in these test piece front faces, bond strength, and a spalling test (it is 10 cycle \*\*\*\*\* trial, using actuation of air cooling as 1 cycle out of a furnace, after heating in the electric furnace currently maintained by 500 degrees C for 20 minutes) It carried out. In addition, what was constructed at conditions with the same said of the sprayed coating of aluminum  $2O_3$  as an example of a comparison and the same process was offered as a sample.

[0026] Table 1 summarizes the test result at this time. The coat which suits this invention is what covered  $2OY_3$  coat directly on the surface of the test piece. (1 No. 3) What began, gave the under coat upwards and formed  $2OY_3$  coat (2 No. 4) Even if all the included coats compare good adhesion and thermal shock resistance with an example and  $2O$ aluminum<sup>3</sup> coat, it is completely equal. Since there is little porosity as compared with the coat of an atmospheric-air spraying process, especially  $2OY_3$  coat formed by the low-pressure-plasma-spraying method can also expect good corrosion resistance.

[0027]

[Table 1]

No.	溶射法	皮膜の構成		気孔率 (%)	密着強さ (MPa)	熱衝撃試験 外観目視	備考
		アンダーコート	トップコート				
1	大気 プラズマ	なし	Y <sub>2</sub> O <sub>3</sub>	5 ~ 9	35 ~ 38	剥離なし	実施例
2		Ni-20Al	Y <sub>2</sub> O <sub>3</sub>	6 ~ 8	38 ~ 41	剥離なし	
3	減圧 プラズマ	なし	Y <sub>2</sub> O <sub>3</sub>	0.2 ~ 3	40 ~ 41	剥離なし	
4		Ni-20Al	Y <sub>2</sub> O <sub>3</sub>	0.3 ~ 4	40 ~ 44	剥離なし	
5	大気 プラズマ	なし	Al <sub>2</sub> O <sub>3</sub>	8 ~ 12	38 ~ 42	剥離なし	比較例
6		Ni-20Al	Al <sub>2</sub> O <sub>3</sub>	9 ~ 12	35 ~ 44	剥離なし	
7	減圧 プラズマ	なし	Al <sub>2</sub> O <sub>3</sub>	0.5 ~ 5	38 ~ 44	剥離なし	
8		Ni-20Al	Al <sub>2</sub> O <sub>3</sub>	0.6 ~ 7	39 ~ 43	剥離なし	

(備考)

- (1) 皮膜厚さ：アンダーコート 100 $\mu$ m、トップコート 300 $\mu$ m  
(2) 密着強さは JIS H8666セラミック溶射皮膜試験方法規定の密着強さ試験法による。  
(3) 熱衝撃試験：500℃×20min →室温（空冷） 繰り返し10回後の外観観察

[0028] In this example, the base material made from aluminum of 50mmx100 mmx5mm thickness is used. an example 2 -- After performing surface treatment as shown in Table 2, a dimension 20mmx20mmx5mm test piece is cut down from each base material. The mask of other parts was carried out so that the range whose surface treatment side is furthermore 10mmx10mm might be exposed, and it irradiated on the following conditions for 20 hours, and the amount of damages by plasma erosion was calculated as thinning thickness.

(1) A gas ambient atmosphere, the flow rate conditions [ CF and Ar ] 4, and the mixed gas of O<sub>2</sub> were made into the ambient atmosphere of the following conditions.

CF<sub>4</sub>/Ar/O<sub>2</sub>= 100/1000/10 ((flow rate cm<sup>3</sup> per for 1 minute)2) Plasma exposure output high-frequency power : 1300 W pressure : 133.3 Pa [0029] The test result was shown in Table 2. Anodic oxide film according to the present technique of the example of a comparison so that clearly from the result shown in this table 2 (No.8) It begins and is B<sub>4</sub>C. Sprayed coating (No.10) It is imagined that is large and the amount of damages by plasma erosion is not all practical. However, it also sets for the example of a comparison. 2Oaluminum<sub>3</sub> sprayed coating (No.9) Comparatively good plasma-proof erosion nature was shown. On the other hand, 2OY<sub>3</sub> sprayed coating of this invention demonstrated the extremely excellent plasma-proof erosion nature, and having maintained the good engine performance under the ambient atmosphere containing a halogenated compound was admitted.

[0030]

[Table 2]

No.	溶射法	表面処理法	アンダーコートの有無	エロージョン損失深さ (μm)	備考
1	Y <sub>2</sub> O <sub>3</sub> (99.9 %)	溶 射	有	6.2	実施例
2			無	6.1	
3	Y <sub>2</sub> O <sub>3</sub> (99.8 %)	溶 射	有	7.6	
4			無	7.2	
5	Y <sub>2</sub> O <sub>3</sub> (99.5 %)	溶 射	有	6.5	
6			無	6.3	
7	Y <sub>2</sub> O <sub>3</sub> (99.9 %)	P V D	無	6.6	比較例
8	Al <sub>2</sub> O <sub>3</sub>	陽極酸化	無	39.5	
9	Al <sub>2</sub> O <sub>3</sub>	溶 射	有	8.1	
10	B <sub>4</sub> C	溶 射	有	28.0	
11	石英	—	無	39.0	

(備考)

- (1) 溶射は大気プラズマ溶射法を用い、アンダーコートの膜厚80μm Y<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>などのトップコートの膜厚は 200μmに成膜
- (2) アンダーコートの材質は80%Ni-20%Al
- (3) 陽極酸化は JIS H8601規定のAA25に準じて成膜させたものである。

[0031] an example 3 -- in this example on the base material made from aluminum of 5mm of width-of-face [ of 50mm ] x die-length 100 mmx thickness as an under coat -- 80%nickel-20%aluminum -- as 80 micrometers and an interlayer aluminum 2O3 -- or -- aluminum2O3 50vol%/Y2O3 50vol% mixture 100 micrometers It is about Y2O3 on it. After forming membranes by the atmospheric-air plasma metal spray method to 200-micrometer thickness, respectively, the plasma erosion trial was carried out on condition that the example 2. Consequently, the sprayed coating of this invention is the maximum surface section.

(topcoat) As long as 2OY3 sprayed coating is formed, it is an interlayer. Even if it arranges aluminum2O3 / [ aluminum 2O3 and ] Y2O3 mixture layer Effect is not received in plasma-proof erosion nature, but it is the exposure of 20 hours. 6.1-7.5 It was admitted that disappearance of mum did not pass to have accepted but demonstrated engine performance sufficient also by the multilayer-structure coat.

[0032] an example 4 -- the base material made from aluminum present in this example -- anodic oxidation (alumite processing) With the test piece carried out It is the alloy coat of 80%nickel-20%aluminum as an under coat on a base material. It covers to 100-micrometer thickness. It is 2OY3 coat as topcoat on it. 250 micrometers of test pieces formed by the plasma metal spray method, respectively are used. Plasma etching was performed on the following conditions and the particle number adhering to the front face of the silicon wafer with a diameter of 8 inches put into the same chamber compared the number of the particle particles which are deleted by etching and disperse. In addition, it investigates with surface-analysis equipment and the adhering particle number is particle size in general. It carried out for the particle 0.2 micrometers or more.

(1) A gas ambient atmosphere and the flow rate conditions CHF3, O2, and Ar were circulated with the respectively following mixing ratios.

CHF3/O2/Ar=80/100/160 ((flow rate cm 3 per for 1 minute)2) Plasma exposure output high-frequency power : 1300 W pressure : 4 Pa temperature : 60 \*\* [0033] It anodizes as a result of this experiment.

(alumite film) In the test piece carried out, 30 of the particle control value 17.5 hours after a plasma exposure and in a general chamber are exceeded, and it is after 25 hours. It became 150 or more pieces. the presentation of this particle -- aluminum and F from -- it was what becoming. On the other hand, by 2OY3



sprayed coating which suits this invention, it became after the 70-hour exposure and the plasma-proof erosion nature which remained and was excellent in extent exceeding a control limit value at last was shown.

[0034]

[Effect of the Invention] The outstanding resistance is shown when it is used under the environment where the plasma erosion operation under the gas ambient atmosphere containing a halogenated compound is received in the member which formed 2OY3 sprayed coating directly on the quality of a metal, or the nature base material of a nonmetal, or constructed the under coat of the quality of a metal upwards, and formed 2OY3 sprayed coating according to this invention, as explained above. For this reason, even if it continues a plasma-etching activity over long duration, the inside of a chamber becomes there is little contamination by particle and possible [ producing a high quality product efficiently ]. Moreover, since the contamination rate by the particle in a chamber becomes slow, spacing of defecation becomes long, improvement in productivity can be expected, and it is very effective as interior material of a plasma treatment container.

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[Translation done.]

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the interior material of a plasma treatment container which is excellent in plasma-proof erosion nature, and its manufacture approach. Especially this invention is a proposal about the technique which it is used, for example, can be applied to DEPOSHIRUDO, a baffle plate, a focal ring, an insulator ring, a shielding ring, bellows covering, an electrode, etc. by plasma treatment in the plasma ambient atmosphere of the raw gas containing a halogen. In addition, this invention is not restricted only to the field of semiconductor fabrication machines and equipment, and can be applied also to plasma treatment container internals, such as a liquid crystal device, again. Hereafter, the example of semiconductor fabrication machines and equipment mainly explains.

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[Translation done.]

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PRIOR ART

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[Description of the Prior Art] general -- manufacture processes, such as a semi-conductor and a liquid crystal device, -- the inside of a processing container -- a \*\*\*\* ghost like BF<sub>3</sub> or NF<sub>3</sub>, and BCl<sub>3</sub> Chlorides, such as SnCl<sub>4</sub>, and HBr like -- in order to use raw gas including a bromide, there was a problem that the interior material of a processing container carried out corrosion consumption remarkably.

[0003] for example, sprayed coatings, such as an anodized film of aluminum covered on metallic materials, such as aluminum and aluminum alloy, and the front face of those as an ingredient currently used in the plasma treatment container of semiconductor fabrication machines and equipment, or boron carbide, and aluminum 2O<sub>3</sub> sintered compact coats, such as Si<sub>3</sub>N<sub>4</sub>, -- macromolecule coats, such as a fluororesin and an epoxy resin, are known further. If these ingredients touch strong corrosive halogen ion, chemical injury is received or receiving erosion damage with particles, such as SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>, and the ion excited by the plasma is known.

[0004] Especially, in the process using a halogenated compound, in order to attain much more activation of a reaction, the plasma is often used. however -- at the same time it dissociates a halogenated compound and it generates F, Cl, corrosive Br, corrosive I, etc. of the shape of a strong atom very much under such a plasma operating environment -- the inside of the environment -- SiO<sub>2</sub> When impalpable powder-like solids, such as Si<sub>3</sub>N<sub>4</sub>, and Si, W, exist, the member used into the plasma treatment container will receive strongly an operation of erosion damages on both by the particle with chemical corrosion. And the environment where the plasma was excited is the phenomenon in which also ionize the gas which does not have corrosive like Ar gas, and this collides to a solid-state side strongly. (ion bombardment) Since it generates, it is also known that the various members currently arranged in the above-mentioned container will receive still stronger damage.

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[Translation done.]

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EFFECT OF THE INVENTION

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[Effect of the Invention] The outstanding resistance is shown when it is used under the environment where the plasma erosion operation under the gas ambient atmosphere containing a halogenated compound is received in the member which formed 2OY3 sprayed coating directly on the quality of a metal, or the nature base material of a nonmetal, or constructed the under coat of the quality of a metal upwards, and formed 2OY3 sprayed coating according to this invention, as explained above. For this reason, even if it continues a plasma-etching activity over long duration, the inside of a chamber becomes there is little contamination by particle and possible [ producing a high quality product efficiently ]. Moreover, since the contamination rate by the particle in a chamber becomes slow, spacing of defecation becomes long, improvement in productivity can be expected, and it is very effective as interior material of a plasma treatment container.

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[Translation done.]

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] Like the semiconductor fabrication machines and equipment mentioned above, there were the following troubles about the following conventional member used in the intense field of chemical corrosion or erosion damage.

(1) aluminum and aluminum alloy are anodized and it has corrosion resistance. 2Oaluminum3 film (alumite) About the ingredient made to generate, when plasma erosion is received in the ambient atmosphere containing halogen gas, there is a problem that a life is short. Moreover, since it is a coat containing aluminum, the particle of  $AlF_3$  occurs and invites the poor product of the semi-conductor to manufacture.

(2) a member front face -- PVD and a CVD method -- the [, such as Sc, Y, La, Ce, Yb, Eu, and Dy, / periodic table ] -- precise coats, such as an oxide of 3a group element, carbide, a nitride, and a \*\*\*\* ghost, are formed, or there is a technique which applies the single crystal of  $Y_2O_3$  (JP,10-4083,A) . However, a membrane formation rate is late inferior to productivity, and also this technique forms two or more coat members in coincidence. (compound coat) There is a fault that it cannot do.

[0006] Then, the purpose of this invention is in the place which proposes the surface treatment member with which the large plasma treatment container of drag force to the damage by the chemical corrosion by environment in which halogen gas is contained, and damage by plasma erosion etc. is presented, and its advantageous manufacture approach.

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[Translation done.]

## MEANS

[Means for Solving the Problem] This invention is conquered by adoption of a solution means to summarize and describe below the problem and fault which the conventional technique is holding and which were mentioned above. That is, it is as follows when the configuration of this invention is arranged.

[0008] (1) It is the covering member in which the layer which consists only of 2OY3 sprayed coating with a% [ of porosity ] of 0.2 - 10 and a thickness of 50-2000 micrometers by the spraying process was formed on the surface of the base material.

[0009] (2) When corrosive [ environmental ] is strong, in under the plasma generating conditions in the ambient atmosphere containing a halogenated compound On the surface of the base material, excelled in adhesion with 2OY3 sprayed coating by the spraying process preferably as an under coat. The coat of one or more sorts of the metal and alloys chosen from nickel and its alloy, W and its alloy, Mo and its alloy, Ti, and its alloy 50-500 It is the covering member which covered in the thickness of mum, and processed 2OY3 sprayed coating into 50-2000-micrometer thickness on the under coat, and formed the compound layer.

[0010] (3) To the front face of a base material, it is a metallic film. (preferably sprayed coating) It is an interlayer on the under coat after constructing as an under coat. Coat of aluminum 2O3 (preferably sprayed coating) It is the covering member which formed and formed further the multilayer-like compound layer which comes to form 2OY3 sprayed coating by thermal spraying as topcoat on the interlayer.

[0011] (4) To the front face of a base material, it is a metallic film. (preferably sprayed coating) It is an interlayer on the under coat after constructing as an under coat. Coat of the mixture of aluminum 2O3 and Y2O3 (preferably sprayed coating) It is the covering member which formed and formed further the multilayer-like compound layer which formed 2OY3 sprayed coating by the spraying process as topcoat on the interlayer.

[0012] (5) 2OY3 sprayed coating which constructed direct or the under coat, and the interlayer and is formed upwards on the surface of a base material [ whether the plasma metal spray of this powder is carried out in atmospheric air by using 2OY3 powder of 95% or more of purity, and ] It is the member which covered the sprayed coating obtained with the application of the thermal-spraying approach which carried out the plasma metal spray under the reduced pressure ambient atmosphere of Ar gas which does not contain oxygen substantially, or was chosen from the high-speed flame-spraying method, the detonation-flame-spraying method, etc. Especially, the approach by low pressure plasma spraying of Ar gas is effective also for a corrosion resistance improvement.

[0013]

[Embodiment of the Invention] As a result of inquiring wholeheartedly about the technical problem which the conventional technique is holding and which was mentioned above according to research of artificers, the damage on the interior material of a plasma treatment container can consider damage by the chemical corrosion by halogen gas, and damage by plasma erosion. When this member was especially used in the ambient atmosphere containing the halogen excited by the plasma, knowledge that it is important just preventing the damage which considers plasma-proof erosion nature as a reason, then it acts effectively also to chemical corrosion prevention was acquired. So, in this invention, it inquired about formation of an effective coat mainly to plasma-proof erosion nature. As the result, the member concerning this invention of upper \*\* was developed.

[0014] That is, fundamentally, this invention adopted as a means of the technical-problem solution was made to form the sprayed coating which consists only of Y2O3 in base material front faces, such as a metal, ceramics, and a carbon material, by the spraying process. And when corrosive [ of the environment where such a member is used ] is strong, while establishing the under coat of the metal in which a strong halogen-proof gas corrosive property is shown in the bottom of said 2OY3 sprayed coating, it is in a pan. It is the approach of also making the interlayer of aluminum Y2O3 [ 2O3 ] preparing and compound-izing. Hereafter, the configuration of this this invention member is explained in detail.

[0015] (1) As a base material set as the construction object of the above-mentioned sprayed coating about a base material, it is the steel, the aluminum and the aluminium alloy, the tungsten and the tungsten alloy, the titanium and the titanium alloy, the molybdenum, the molybdenum alloy, the carbon, and the oxide system of the various kinds containing stainless steel, A non-oxide system ceramic sintered compact or a carbonaceous ingredient is suitable. In addition, since copper and a copper alloy are emitted by the corrosive action by plasma erosion or the halogenated compound and cause environmental pollution, they are not

desirable. Therefore, constitutionally, when [ of equipment ] copper and a copper alloy need to be used, means, such as electroplating, chemical plating, and vacuum evaporation, need to cover with Cr, nickel, etc.

[0016] (2) [ whether about a coat configuration, after formation of a coat on the above-mentioned base material front face carries out blasting processing of the base material, it carries out thermal spraying of  $Y_2O_3$  directly, and forms membranes, and ] Or the approach of PVD processing, CVD-processing or thermal-spraying processing, and forming in a base material front face the coat which consists of a strong halogen-proof gas corrosive metallic material as an under coat layer first, and using  $2OY_3$  powder as topcoat, it carrying out thermal spraying on the under coat, and using as a compound layer is desirable. In this case, said metal under coat s (sprayed coating etc.) Thickness is 50-500. It considers as within the limits of mum. When an under coat layer is thinner than 50 micrometers, the operation effectiveness as an under coat is weak, and on the other hand, it is 500. Since effectiveness is saturated with the thickness exceeding mum, there is no semantics of the tylosis, and it is because it is not a best policy. As this metallic material for under coats, nickel and a nickel alloy, a tungsten and a tungsten alloy, molybdenum and a molybdenum alloy, titanium, a titanium alloy, etc. are suitable.

[0017] on the other hand, construct  $2OY_3$  sprayed coating used as topcoat directly on a base material front face -- moreover, carry out thermal spraying on said under coat, and make it a compound layer -- further -- as an interlayer aluminum  $2O_3$  the case where  $2O_{aluminum}2O_3+Y_3$  coat is prepared -- be -- it is desirable to construct in thickness of 50-2000 micrometers anyway. The reason is that effectiveness saturates and is not more economical than 50 micrometers in a film even if effectiveness is scarce and makes it thicker than 2000 micrometers on the other hand to prevention of damage by plasma erosion.

[0018] In addition, the porosity of  $2OY_3$  sprayed coating of topcoat has 0.5 - 10% of good range. 0.5 In a spraying process, the coat below % is difficult to manufacture, and is because it is inferior to corrosion resistance and plasma-proof erosion nature in the coat of 10% or more of porosity.

[0019] (3) About  $2OY_3$  sprayed coating of a member maximum surface layer, the configuration of this invention by which it is characterized most adopts  $Y_2O_3$  as an ingredient in which plasma-proof erosion nature is shown in the ambient atmosphere which contains halogen gas for the maximum surface of a base material, and is in the place which carries out covering formation by making this into a thermal-spraying layer. Namely, as for  $Y_2O_3$ , according to research of this invention, it turned out that it maintains the condition of having been stabilized even if specific gravity receives a plasma erosion operation in the ambient atmosphere in which it is 2410 degrees C, and 4.84 and the melting point contain halogen gas since chemical bonding strength with oxygen is strong. However, this  $2OY_3$  purity needs to use 95% or more of thing, and if impurities, such as Fe, Mg, Cr, aluminum, nickel, and Si, are contained as oxide, since erosion-proof nature will fall, it is not desirable. The thing of 98% or more of purity is more desirable. In addition, interlayer who makes it form directly under this  $2OY_3$  sprayed coating A chemically stable top, as for aluminum  $2O_3$ , there is little change under an atmospheric-air plasma metal spray or a low-pressure-plasma-spraying environment, and it bears the operation which compensates the plasma-proof erosion nature of  $Y_2O_3$ .

[0020] (4) Let  $2OY_3$  coat of the maximum surface topcoat at least be a sprayed coating in formation this invention of a covering approach a. sprayed coating. And it is the semantics which strengthens this coat further under this topcoat sprayed coating preferably, and it is desirable to make the whole coat configuration into the following multilayer structure. That is, after constructing the under coat of a metallizing coat on the surface of a base material,  $2O_{aluminum}3$  sprayed coating or inclination combination is started on it. A mixture sprayed coating with aluminum  $2O_3$  and  $Y_2O_3$  is constructed as an interlayer, and  $2OY_3$  sprayed coating is further formed as topcoat on it. The reason nil why such a coat configuration is desirable is excellent in corrosion resistance and plasma-proof erosion nature as compared with a metallizing coat. It is because a sprayed coating can be multilayer-structure-ized, penetration pore of a coat can be lessened and corrosion resistance and erosion-proof nature can be raised by forming aluminum  $2O_3$  as an interlayer. And it is as an interlayer. Adhesion with both an under coat and topcoat good [ aluminum  $2O_3$  ] is demonstrated. In this semantics, it is more desirable to consider as an interlayer and the layer of mixture with aluminum  $2O_3$  and  $Y_2O_3$ , and it is an under coat side in this case. While making  $2O_{aluminum}3$  concentration high, in a topcoat side, it is desirable to consider as the mixolimnion concerning inclination combination to which  $2OY_3$  concentration becomes high. Since such an interlayer's formation can be easily constructed if a spraying process is adopted, it can be called desirable operation

gestalt that an interlayer is formed as a sprayed coating. In addition, the same range as 2OY3 sprayed coating of topcoat is suitable for an interlayer's thickness.

[0021] It sets to this invention and is a metal. Although an atmospheric-air plasma metal spray method or the plasma metal spray method in the inside of the ambient atmosphere which does not contain oxygen substantially is suitable in order to form aluminum 2O3 and the sprayed coating of Y2O3, construction by high-speed flame spraying or the detonation-flame-spraying method is also possible.

[0022] b. Under coat by the CVD method and PVD, Although a reduction deposit is carried out by hydrogen etc. and the steam of a necessary metal halogenated compound is oxidized with oxygen or an oxygen compound after that in an interlayer's formation CVD method, membranes are formed by making it change to an oxide film by heating in atmospheric air. On the other hand, in PVD, a sintered compact or powder is used as a raw material, in this, an electron beam is irradiated, and is vaporized, and membranes are formed by depositing this on a base material front face. Formation of the coat generally according to a CVD method and PVD is a thin film. (for example, before or after 50 micrometers) It is suitable for construction.

[0023] (5) 2OY3 sprayed coating covered on the member front face which starts this invention about the operating environment of the member concerning this invention is useful especially when using it under the plasma environment generated under the ambient atmosphere containing a halogenated compound.

[0024] Of course, since erosion damage is loose as compared with the ambient atmosphere which is effective as for this invention and contains a halogen especially in this case also to the plasma erosion operation under ambient atmospheres, such as N2 which does not contain a halogen or a halogenated compound, and H2, the coat covering member concerning this invention demonstrates the engine performance stabilized over the long period of time.

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[Translation done.]



## EXAMPLE

[Example] an example 1 -- this example -- test piece made from aluminum (dimension: 5mm of 50mm x thickness of width-of-face [ of 50mm ] x length) 2OYafter carrying out surface roughening of one side by blasting processing3 thermal spray material -- using -- an atmospheric-air plasma metal spray method and Ar gas -- the ambient pressure force -- 50 - 200 hPa the controlled low-pressure-plasma-spraying method -- respectively -- thickness 300 mY2Omu3 sprayed coating was formed. Moreover, it is thickness 100 about the under coat of a nickel-20%aluminum alloy by the atmospheric-air plasma metal spray method to one side of the test piece made from aluminum. It is 300, using said Y2O3 as topcoat, after constructing to mum thickness. What was covered to mum thickness was produced. Then, the porosity of 2OY3 sprayed coating currently formed in these test piece front faces, bond strength, and a spalling test (it is 10 cycle \*\*\*\*\* trial, using actuation of air cooling as 1 cycle out of a furnace, after heating in the electric furnace currently maintained by 500 degrees C for 20 minutes) It carried out. In addition, what was constructed at conditions with the same said of the sprayed coating of aluminum 2O3 as an example of a comparison and the same process was offered as a sample.

[0026] Table 1 summarizes the test result at this time. The coat which suits this invention is what covered 2OY3 coat directly on the surface of the test piece. (1 No. 3) What began, gave the under coat upwards and formed 2OY3 coat (2 No. 4) Even if all the included coats compare good adhesion and thermal shock resistance with an example and 2Oaluminum3 coat, it is completely equal. Since there is little porosity as compared with the coat of an atmospheric-air spraying process, especially 2OY3 coat formed by the low-pressure-plasma-spraying method can also expect good corrosion resistance.

[0027]

[Table 1]

No	溶射法	皮膜の構成		気孔率 (%)	密着強さ (MPa)	熱衝撃試験 外観目視	備考
		アンダーコート	トップコート				
1	大気 プラズマ	なし	Y <sub>2</sub> O <sub>3</sub>	5 ~ 9	35 ~ 38	剥離なし	実施例
2		Ni-20Al	Y <sub>2</sub> O <sub>3</sub>	6 ~ 8	38 ~ 41	剥離なし	
3	減圧 プラズマ	なし	Y <sub>2</sub> O <sub>3</sub>	0.2 ~ 3	40 ~ 41	剥離なし	
4		Ni-20Al	Y <sub>2</sub> O <sub>3</sub>	0.3 ~ 4	40 ~ 44	剥離なし	
5	大気 プラズマ	なし	Al <sub>2</sub> O <sub>3</sub>	8 ~ 12	38 ~ 42	剥離なし	比較例
6		Ni-20Al	Al <sub>2</sub> O <sub>3</sub>	9 ~ 12	35 ~ 44	剥離なし	
7	減圧 プラズマ	なし	Al <sub>2</sub> O <sub>3</sub>	0.5 ~ 5	38 ~ 44	剥離なし	
8		Ni-20Al	Al <sub>2</sub> O <sub>3</sub>	0.6 ~ 7	39 ~ 43	剥離なし	

(備考)

(1) 皮膜厚さ：アンダーコート 100μm、トップコート 300μm

(2) 密着強さは JIS H8666セラミック溶射皮膜試験方法規定の密着強さ試験法による。

(3) 熱衝撃試験：500℃×20min → 室温 (空冷) 繰り返し10回後の外観観察

[0028] In this example, the base material made from aluminum of 50mmx100 mmx5mm thickness is used. an example 2 -- After performing surface treatment as shown in Table 2, a dimension 20mmx20mmx5mm test piece is cut down from each base material. The mask of other parts was carried out so that the range whose surface treatment side is furthermore 10mmx10mm might be exposed, and it irradiated on the following conditions for 20 hours, and the amount of damages by plasma erosion was calculated as thinning thickness.

(1) A gas ambient atmosphere, the flow rate conditions [ CF and Ar ] 4, and the mixed gas of O<sub>2</sub> were made into the ambient atmosphere of the following conditions.

CF<sub>4</sub>/Ar/O<sub>2</sub>= 100/1000/10 ((flow rate cm<sup>3</sup> per for 1 minute)2) Plasma exposure output high-frequency

power : 1300 W pressure : 133.3 Pa [0029] The test result was shown in Table 2. Anodic oxide film according to the present technique of the example of a comparison so that clearly from the result shown in this table 2 (No.8) It begins and is B<sub>4</sub>C. Sprayed coating (No.10) It is imagined that is large and the amount of damages by plasma erosion is not all practical. However, it also sets for the example of a comparison. 2Oaluminum3 sprayed coating (No.9) Comparatively good plasma-proof erosion nature was shown. On the other hand, 2OY3 sprayed coating of this invention demonstrated the extremely excellent plasma-proof erosion nature, and having maintained the good engine performance under the ambient atmosphere containing a halogenated compound was admitted.

[0030]

[Table 2]

No.	溶射法	表面処理法	アンダーコートの有無	エロージョン損失深さ (μm)	備考
1	Y <sub>2</sub> O <sub>3</sub> (99.9 %)	溶 射	有	6.2	実施例
2			無	6.1	
3	Y <sub>2</sub> O <sub>3</sub> (99.8 %)	溶 射	有	7.6	
4			無	7.2	
5	Y <sub>2</sub> O <sub>3</sub> (99.5 %)	溶 射	有	6.5	
6			無	6.3	
7	Y <sub>2</sub> O <sub>3</sub> (99.9 %)	PVD	無	6.6	比較例
8	Al <sub>2</sub> O <sub>3</sub>	陽極酸化	無	39.5	
9	Al <sub>2</sub> O <sub>3</sub>	溶 射	有	8.1	
10	B <sub>4</sub> C	溶 射	有	28.0	
11	石英	—	無	39.0	

(備考)

- (1) 溶射は大気プラズマ溶射法を用い、アンダーコートの膜厚80μm Y<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>などのトップコートの膜厚は 200μmに成膜
- (2) アンダーコートの材質は80%Ni-20%Al
- (3) 陽極酸化は JIS H8601規定のAA25に準じて成膜させたものである。

[0031] an example 3 -- in this example on the base material made from aluminum of 5mm of width-of-face [ of 50mm ] x die-length 100 mmx thickness as an under coat -- 80%nickel-20%aluminum -- as 80 micrometers and an interlayer aluminum 2O3 -- or -- aluminum2O3 50vol%/Y2O3 50vol% mixture 100 micrometers It is about Y2O3 on it. After forming membranes by the atmospheric-air plasma metal spray method to 200-micrometer thickness, respectively, the plasma erosion trial was carried out on condition that the example 2. Consequently, the sprayed coating of this invention is the maximum surface section. (topcoat) As long as 2OY3 sprayed coating is formed, it is an interlayer. Even if it arranges aluminum2O3 / [ aluminum 2O3 and ] Y2O3 mixture layer Effect is not received in plasma-proof erosion nature, but it is the exposure of 20 hours. 6.1-7.5 It was admitted that disappearance of mum did not pass to have accepted but demonstrated engine performance sufficient also by the multilayer-structure coat.

[0032] an example 4 -- the base material made from aluminum present in this example -- anodic oxidation (alumite processing) With the test piece carried out It is the alloy coat of 80%nickel-20%aluminum as an under coat on a base material. It covers to 100-micrometer thickness. It is 2OY3 coat as topcoat on it. 250 micrometers of test pieces formed by the plasma metal spray method, respectively are used. Plasma etching was performed on the following conditions and the particle number adhering to the front face of the silicon wafer with a diameter of 8 inches put into the same chamber compared the number of the particle particles

which are deleted by etching and disperse. In addition, it investigates with surface-analysis equipment and the adhering particle number is particle size in general. It carried out for the particle 0.2 micrometers or more.

(1) A gas ambient atmosphere and the flow rate conditions CHF<sub>3</sub>, O<sub>2</sub>, and Ar were circulated with the respectively following mixing ratios.

CHF<sub>3</sub>/O<sub>2</sub>/Ar=80/100/160 ((flow rate cm<sup>3</sup> per for 1 minute)2) Plasma exposure output high-frequency power : 1300 W pressure : 4 Pa temperature : 60 °C [0033] It anodizes as a result of this experiment.

(alumite film) In the test piece carried out, 30 of the particle control value 17.5 hours after a plasma exposure and in a general chamber are exceeded, and it is after 25 hours. It became 150 or more pieces. the presentation of this particle -- aluminum and F from -- it was what becoming. On the other hand, by 2OY3 sprayed coating which suits this invention, it became after the 70-hour exposure and the plasma-proof erosion nature which remained and was excellent in extent exceeding a control limit value at last was shown.

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[Translation done.]



## TRANSLATOR CERTIFICATION

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Morningside | Translations

I, John Marchioro, a translator fluent in the Japanese language, on behalf of Morningside Evaluations and Consulting, do solemnly and sincerely declare that the following is, to the best of my knowledge and belief, a true and correct translation of the document(s) listed below in a form that best reflects the intention and meaning of the original text.

### MORNINGSIDE EVALUATIONS AND CONSULTING

  
Signature of Translator

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(54) [Title of the Invention] The inner material of a plasma processing container and the method for manufacturing the same

(57) [Abstract]

[Problem] To propose an inner material of a plasma processing container with excellent plasma erosion resistance, and the method for manufacturing the same.

[Means of Solution] The surface of the base materials is coated by a multi-layer composite laminate composed of a metal coating that is formed as an undercoat, an  $\text{Al}_2\text{O}_3$  coating that is formed as an intermediate layer on this undercoat, and a  $\text{Y}_2\text{O}_3$  sprayed coating that is formed as a topcoat on this intermediate layer.

[Scope of Patent Claims]

[Claim 1] An inner material of a plasma processing container, wherein the surface of the base material is coated by  $Y_2O_3$  sprayed coating.

[Claim 2] The inner material of a plasma processing container described in Claim 1, wherein it has a metal layer as an undercoat under the  $Y_2O_3$  sprayed coating that is formed as a topcoat.

[Claim 3] The inner material of a plasma processing container described in Claim 2, wherein it has an intermediate layer between the metal coating that is formed as an undercoat and the  $Y_2O_3$  sprayed coating that is formed as a topcoat.

[Claim 4] The inner material of a plasma processing container described in Claim 2 or 3, wherein the metal coating, which is the undercoat, is a coating that is formed to a thickness of 50~500  $\mu m$  with one or more kinds of metal or alloy selected from Ni and the alloys thereof, W and the alloys thereof, Mo and the alloys thereof and Ti and the alloys thereof.

[Claim 5] The inner material of a plasma processing container described in Claim 3, wherein the intermediate layer has been formed with  $Al_2O_3$  or a mixed coating of  $Al_2O_3$  and  $Y_2O_3$ .

[Claim 6] The inner material of a plasma processing container described in Claim 5, wherein the intermediate layer composed of a mixed coating of  $Al_2O_3$  and  $Y_2O_3$  is a layer that has a graduated concentration wherein the concentration of  $Al_2O_3$  is high on the undercoat side and the concentration of  $Y_2O_3$  is high on the topcoat side.

[Claim 7] The inner material of a plasma processing container described in any one of the claims from Claim 1 to 5, wherein the porosity of the  $Y_2O_3$  sprayed coating is within a range of 0.5~10%, and the coating thickness is in a range of 50~2,000  $\mu m$ .

[Claim 8] A method for manufacturing the inner material of a plasma processing container, wherein the surface of the base material is coated with  $Y_2O_3$  by the spray method, and a  $Y_2O_3$  sprayed coating is formed thereby.

[Claim 9] A method for manufacturing the inner material of a plasma processing container, wherein one or more surface processing methods selected from the CVD method, PVD method and spray method is applied to the surface of the base material, the base material is coated with a metal composed of Ni, W, Mo or Ti, and the alloys thereof as an undercoat, and then a composite laminate is formed by coating this undercoat with  $Y_2O_3$  as a topcoat.

[Claim 10] A method for manufacturing the inner material of a plasma processing container, wherein one or more surface processing methods selected from the CVD method, PVD method and spray method is applied to the surface of the base material to form an undercoat, and next an intermediate layer is formed on this undercoat by coating the latter with  $Al_2O_3$  or a mixture of  $Al_2O_3$  and  $Y_2O_3$ , after which a topcoat is formed on this intermediate layer by coating the latter with  $Y_2O_3$ .

[Detailed Explanation of the Invention]

[0001]

[Technical Field to which the Invention Pertains]

The present invention relates to an inner material of a plasma processing container with excellent plasma erosion resistance, and the method for manufacturing the same. In particular, the present invention is a proposal about a technique that is used in plasma

processing in a plasma atmosphere of processing gas containing halogen elements, and that can be applied for example to deposition shields, baffle plates, focus rings, insulator rings, shield rings, bellows covers, electrodes, etc. In addition, the present invention is not limited solely to the field of semiconductor manufacturing apparatuses, and can also be applied to the products inside plasma processing containers such as liquid crystal devices. The description below is provided chiefly with reference to semiconductor manufacturing apparatuses.

[0002]

[Prior Art] In general, processing gas, beginning with such things as fluorides like  $\text{BF}_3$  and  $\text{NF}_3$ , chlorides like  $\text{BCl}_3$  and  $\text{SnCl}_4$ , and bromides like  $\text{HBr}$  are used in the processing container, in the manufacturing process of such items as semiconductors and liquid crystal devices, and there is the problem that the inner material of the processing container is markedly corroded and subjected to attrition.

[0003] The following are known of for example as materials that are used inside the plasma processing containers of semiconductor manufacturing apparatuses: metal materials such as Al and Al alloys, anodic oxidation coatings of that are coated on the surface thereof, or sprayed coatings such as boron carbide, sintered compact coatings of  $\text{Al}_2\text{O}_3$  and  $\text{Si}_3\text{N}_4$ , and macromolecular coatings of fluoride resin or epoxy resin. It is known that when these materials come into contact with highly corrosive halogen ions, they undergo chemical damage, and suffer erosion damage due to the fine particles of  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  and the ions that are excited by the plasma.

[0004] In particular, plasma is frequently used in order to provide for further activation of the reactions in processes that employ halogen compounds. However, when in such plasma use environments the fine powder solids of  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$ , Si, W, etc., are present in the environment at the same time as the halogen compounds disassociate and produce extremely corrosive F, Cl, Br and I in molecular form, the members that are employed inside the plasma processing container are strongly subjected to the double action of chemical corrosion and erosion loss due to fine particles. Moreover, it is known that an environment excited by plasma is ionized by non-corrosive gasses such as Ar gas, and a phenomenon wherein this strongly collides with a solid surface (ion bombardment) occurs, so the various members disposed inside the above-mentioned container are subjected to still stronger damage.

[0005]

[Problems that the Invention Attempts to Solve] There are the following problems in the conventional members described below that are employed in fields where there is serious chemical corrosion and erosion damage, such as the above-described semiconductor manufacturing apparatuses.

(1) There is the problem that materials that subject Al and Al alloys to anodic oxidation and produce an corrosion-resistant  $\text{Al}_2\text{O}_3$  coating (alumite) are subjected to plasma erosion and have a short lifespan in an atmosphere that contains a halogen gas. In addition, since it is a coating that contains Al, particles of  $\text{AlF}_3$  are produced, and this leads to defects in the semiconductor products that are manufactured.

(2) There is a technique whereby a fine coating of the oxides, carbides, nitrides, fluorides, etc., of the 3a group of elements of the periodic table such as Sc, Y, La, Ce, Yb, Eu and Dy is formed on the member surface by the PVD method or CVD method, and a monocrystal of  $\text{Y}_2\text{O}_3$  is applied thereto (Japanese Public Patent Disclosure Bulletin No.



H10-4083). However, this technique has the drawback that the speed of coating formation is slow and it is inferior in productivity, and in addition it is not possible to form multiple coating members (a composite coating) at the same time.

[0006] Accordingly, the purpose of the present invention is propose a surface processing member provided for plasma processing containers, etc., which has great resistance to damage due to chemical corrosion due to environments like those containing halogen gas and to damage due to plasma erosion, and a beneficial method for manufacturing the same.

[0007]

[Means for Solving the Problems] The present invention overcomes the above-described problems and drawbacks harbored by the prior art by the adoption of the means of solution that is summarized and described below. That is, one can recount the composition of the present invention as follows.

[0008] (1) It is a coated member, wherein the surface of the base material is coated with a layer composed of only a  $Y_2O_3$  sprayed coating with a porosity of 0.2~10% and a thickness of 50~2,000  $\mu m$  by the spray method.

[0009] It is a coated member, wherein in the event that the corrosiveness of the environment is strong, for example, in the case where it is under conditions of plasma generation in an atmosphere that contains halogen compounds, a coating composed of one or more kind of metal or alloy selected from Ni and the alloys thereof, W and the alloys thereof, Mo and the alloys thereof and Ti and the alloys thereof, which have excellent adhesion with a  $Y_2O_3$  spray coating, is formed as an undercoat on the surface of the base material preferably by the spray method, and the latter is coated to a thickness of 50~500  $\mu m$ , and then a  $Y_2O_3$  spray coating is added to a thickness of 50~2,000  $\mu m$  and a composite lamination is formed on this undercoat thereby.

[0010] (3) A coated member that forms a multi-layer composite lamination, wherein a metal coating is applied as an undercoat (preferably a spray coating) to the surface of the base material, after which a coating of  $Al_2O_3$  is formed as an intermediate layer (preferably by the spray method) on this undercoat, and then a  $Y_2O_3$  spray coating is formed by spraying as a topcoat on this intermediate layer.

[0011] (4) A coated member that forms a multi-layer composite lamination, wherein a metal coating is applied as an undercoat (preferably a spray coating) to the surface of the base material, after which a coating composed of a mixture of  $Al_2O_3$  and  $Y_2O_3$  is formed as an intermediate layer (preferably by the spray method) on this undercoat, and then a  $Y_2O_3$  spray coating is formed by spraying as a topcoat on this intermediate layer.

[0012] (5) A member wherein the surface of the base material is coated with a  $Y_2O_3$  spray coating is formed directly thereon or after processing an undercoat or intermediate layer, and this spray coating is obtained by using  $Y_2O_3$  with a purity of 95% and above and either plasma spraying the powder thereof in the atmosphere or plasma spraying under a reduced pressure atmosphere of Ar gas that essentially does not contain oxygen, or applying a spraying method selected from high-speed flame spraying, explosion spraying, etc. Of these, the method based on reduced pressure plasma spraying of Ar gas is also effective in the improvement of corrosiveness.

[0013]

[Mode of Embodiment of the Invention] According to the research of the inventors, the result of their painstaking study of the above-mentioned problems harbored by the prior

art is that the damage to the inner material of the plasma processing container may be due to damage due to plasma erosion. In particular, they found that in the event that this member is used in an atmosphere that contains halogen that is excited by plasma, what is important is preventing damage, and plasma erosion resistance is the source of the solution thereto, and this being so this also acts effectively in the prevention of chemical corrosion. Accordingly, in this invention the inventors chiefly undertook research about the formation of a coating that is effective for plasma erosion resistance. They developed the above-described member for the present invention as the result thereof.

[0014] That is, as the means for solving these problems, they decided to form sprayed coating composed of only  $Y_2O_3$ , by the spray method, on the surface of the base material, which is metal, ceramic, a carbon material, etc. Then, this is a method wherein, in those cases where the corrosiveness of the environment in which such a member is used is strong, an undercoat of metal that exhibits properties of strong resistance to halogen corrosion is provided under the above-mentioned  $Y_2O_3$  sprayed layer, and in addition it is further compounded by providing an intermediate layer of  $Al_2O_3$  or  $Y_2O_3$ . A detailed description is provided below of said member for the present invention.

[0015] (1) About the base material

The following are optimal as the base material that serves as the object of the processing with the above-mentioned sprayed coating: Various kinds of steel including stainless steel, aluminum and aluminum alloys, tungsten and tungsten alloys, titanium and titanium alloys, molybdenum and molybdenum alloys, and carbon, as well as oxide or non-oxide ceramic sintered compacts, or carbonaceous materials. Since copper and copper alloys are emitted by plasma erosion and corrosive action due to halogen compounds, and this becomes a cause of environmental pollution, these are not desirable. Therefore, in the event that it is necessary to use copper and copper alloys in terms of the composition of an apparatus, it is necessary to coat these with Cr, Ni, etc., by a means such as electroplating, chemical plating, vapor deposition, etc.

[0016] (2) About the coating composition

As far as the formation of a coating on the above-mentioned base material surface is concerned, it is preferable that this be done by a method wherein the  $Y_2O_3$  is sprayed directly on the base material and the coating is formed thereon, after the base material has been subjected to plasma processing, or a coating composed of a metal material that is strongly resistant to halogen corrosion is first formed as an undercoat on the base material surface by PVD processing, CVD processing or spray processing, and then a composite lamination is made by spraying  $Y_2O_3$  powder on this undercoat as a topcoat. In this case, the coating thickness of the above-mentioned metal undercoat (sprayed coating, etc.) is set within a range of 50~500  $\mu m$ . This is because when the undercoat layer is thinner than 50  $\mu m$ , its action and effects as an undercoat are weak, and when on the other hand its thickness exceeds 500  $\mu m$  the effects are saturated, so there is no sense in making the layer overly thick, and this is not advisable. The following are optimal as the metal materials used for said undercoat: Nickel and nickel alloys, tungsten and tungsten alloys, molybdenum and molybdenum alloys, titanium and titanium alloys, etc.

[0017] On the other hand, it is preferable that the  $Y_2O_3$  sprayed coating that serves as the topcoat is in any event is processed to a thickness of 50-2,000  $\mu m$ , in the event it is something that is directly added to the base material surface and is further made into a composite lamination by spraying it on the above-mentioned undercoat, and a  $Al_2O_3$  or

$\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  coating is provided as an intermediate layer. The reason for this is that the effects on prevention of damage due to plasma erosion are weak when the thickness is less than 50  $\mu\text{m}$ , while the effects are saturated and it is not economical when it is greater than 2,000  $\mu\text{m}$ .

[0018] It is best that the porosity of the  $\text{Y}_2\text{O}_3$  sprayed coating of the topcoat is in a range of 0.5~10%. This is because it is difficult to manufacture a coating with a porosity of less than 0.5% by the spray method, while a coating with a porosity of over 10% is inferior in its resistance to corrosion and plasma erosion.

[0019] (3) About the  $\text{Y}_2\text{O}_3$  sprayed coating of the uppermost surface layer of the member The composition is most characteristic of the present invention is that  $\text{Y}_2\text{O}_3$  is adopted as the material that exhibits plasma erosion resistance in an atmosphere that contains a halogen gas, for the uppermost surface layer of the base material, and this is formed by coating as a sprayed layer. In other words, according to the research for the present invention, it was learned that since the specific gravity of  $\text{Y}_2\text{O}_3$  is 4.84 and its melting point is 2,410 degrees Centigrade, and it has strong chemical bonding force with oxygen, it maintains a stable state even if it is subjected to plasma erosion action in an atmosphere that contains a halogen gas. However, it is necessary to employ  $\text{Y}_2\text{O}_3$  with purity of 95% and above, and when impurities such as Fe, Mo, Cr, Al, Ni and Si are contained as oxides, the resistance to erosion declines, and this is not desirable.  $\text{Y}_2\text{O}_3$  whose purity is 98% and above is preferable, and given the fact that the  $\text{Al}_2\text{O}_3$  of the intermediate layer that is formed directly under this  $\text{Y}_2\text{O}_3$  sprayed coating is chemically stable, there is little change even under atmospheric plasma spraying and subatmospheric plasma spraying environments, and this is responsible for effects that compensate for the plasma erosion resistance of  $\text{Y}_2\text{O}_3$ .

[0020] Coating method

a. Formation of the sprayed coating

In the present invention, the  $\text{Y}_2\text{O}_3$  coating of at least the uppermost surface layer topcoat is to be a sprayed layer. Then, it is preferable that the overall coating composition be made into a multi-layer structure like that below, in terms of further strengthening preferably this coating under the topcoat sprayed layer. That is, after the undercoat of the metal sprayed coating is applied to the surface of the base material, an  $\text{Al}_2\text{O}_3$  sprayed coating or a mixed sprayed coating of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  for the graduated compounded is applied as an intermediate layer on this, and a  $\text{Y}_2\text{O}_3$  sprayed coating is moreover formed as a topcoat on this. The reason why such a coating composition is desirable is that by forming as an intermediate layer  $\text{Al}_2\text{O}_3$ , which is superior in corrosion resistance and plasma erosion resistance compared to metal sprayed coatings, the sprayed coatings are made into a multi-layer structure, and it is possible to decrease the number of air holes that pass through the coating and to improve the erosion resistance thereby. Moreover, as an intermediate layer  $\text{Al}_2\text{O}_3$  has excellent adhesion with both the undercoat and the topcoat. In this sense, it is more desirable to make the intermediate layer a layer composed of a mixture of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ , and in this case it is preferable to make it a mixed layer for graduated compounding such that the  $\text{Al}_2\text{O}_3$  concentration on the undercoat side is increased while the  $\text{Y}_2\text{O}_3$  concentration becomes higher on the topcoat side. The formation of such an intermediate layer can be executed easily if the spray method is employed, one can say that forming an intermediate layer as a spray coating is

a preferred embodiment. It is optimal if the thickness of the intermediate layer is in the same range as that of the  $Y_2O_3$  sprayed coating of the topcoat.

[0021] In the present invention, the atmospheric plasma spray method or a spray method in an atmosphere that essentially does not contain oxygen is optimal in order to form the sprayed coatings made of metal,  $Al_2O_3$  or  $Y_2O_3$ , but it is also possible to execute this by high speed flame spraying or explosion spraying.

[0022] b. Formation of the undercoat and the intermediate layer by the CVD method and PVD method

In the CVD method, the vapor of the required metal halogen compound is reduced and deposited by hydrogen, etc., after which it is oxidized by oxygen or an oxygen compound, but the coating is formed by altering this to an oxide coating, by heating it in the atmosphere. On the other hand, in the PVD method, a sintered compact or powder is employed as the raw materials, and the coating is formed by volatilizing this with irradiation with an electron beam, and depositing this on the surface of the base material. In general, the formation of coatings by the CVD method and PVD method is suitable for the formation of thin coatings (for example, about 50  $\mu m$ ).

[0023] (5) About the use environment of the member for the present invention

The  $Y_2O_3$  sprayed coating that is coated onto the member surface for the present invention is particularly useful in event that it is used in a plasma environment that is generated under an atmosphere that contains halogen compounds.

[0024] Naturally, the present invention is also effective against plasma erosion action under an atmosphere of  $N_2$ ,  $H_2$ , etc., that does not contain halogen atoms or halogen compounds, and since in this case the erosion damage is moderate compared with atmospheres that contain a halogen in particular, the member covered with a coating for the present invention displays a stable performance over a long period of time.

[0025]

[Embodiment] Embodiment 1

In this embodiment, one surface of a test piece made of aluminum (dimensions: 50 mm wide x 50 mm long x 5 mm thick) was made into a rough surface by blast treatment, after which  $Y_2O_3$  sprayed coatings with a coating thickness of 300  $\mu m$  were formed respectively by the atmospheric plasma spray method, and a subatmospheric plasma spray method that controlled the atmospheric pressure to 50~200 hPa with Ar gas, with the  $Y_2O_3$  sprayed material. In addition, an undercoat of Ni-20% Al alloy was applied to a thickness of 100  $\mu m$  by the atmospheric plasma spray method, on one side of the aluminum test pieces, after which items that were coated with the above-mentioned  $Y_2O_3$  to a thickness of 300  $\mu m$  as a topcoat were prepared. After that, porosity, adhesion strength and thermal shock tests (a test in which 1 cycle involved heating the pieces for 20 minutes in an electric furnace that is kept at 500 degrees Centigrade, after which an air-cooling operation outside the furnace is performed; 10 such cycles are repeated in this test) were conducted. As comparative examples,  $Al_2O_3$  sprayed coatings to which the same process was applied under the same conditions were supplied for the tests.

[0026] Figure 1 summarizes the test results at this time. When it comes to the coatings that conform to the present invention, all the coatings, beginning with the items (Nos. 1 and 3) in which the surface of the test piece was coated directly with a  $Y_2O_3$  coating and including those items (No. 2, 4) wherein a  $Y_2O_3$  coating was formed after an undercoat was applied, exhibited excellent adhesion and thermal shock resistance, and compared

favorably with the  $\text{Al}_2\text{O}_3$  coatings. In particular, since the porosity of the  $\text{Y}_2\text{O}_3$  coatings formed by the subatmospheric plasma spray method was less than that of the coatings formed by the atmospheric spray method, it is possible to anticipate good corrosion resistance for the former.

[0027]

[Table 1]

No.	Spraying method	Composition of coating		Porosity (%)	Adhesion strength (MPa)	Thermal shock test Visual observation of appearance	Remarks
		Undercoat	Topcoat				
1	Atmospheric plasma	None	$\text{Y}_2\text{O}_3$	5~9	35~38	No peeling	Embodiments
2		Ni-20Al	$\text{Y}_2\text{O}_3$	6~8	38~41	No peeling	
3	Subatmospheric plasma	None	$\text{Y}_2\text{O}_3$	0.2~3	40~41	No peeling	
4		Ni-20Al	$\text{Y}_2\text{O}_3$	0.3~4	40~44	No peeling	
5	Atmospheric plasma	None	$\text{Al}_2\text{O}_3$	8~12	38~42	No peeling	Comparative examples
6		Ni-20Al	$\text{Al}_2\text{O}_3$	9~12	35~44	No peeling	
7	Subatmospheric plasma	None	$\text{Al}_2\text{O}_3$	0.5~5	38~44	No peeling	
8		Ni-20Al	$\text{Al}_2\text{O}_3$	0.6~7	39~43	No peeling	

(1) Coating thickness: Undercoat 100  $\mu\text{m}$ , topcoat 300  $\mu\text{m}$

(2) The adhesion strength is based on the adhesion strength test method that is prescribed as the ceramic sprayed coating test method in JIS H8666.

(3) Thermal shock test: 500 degree Centigrade x 20 minutes → Air temperature (air cooling). This is repeated 10 times, after which observations are made of the appearance.

#### [0028] Embodiment 2

In this embodiment, surface processing like that shown in Table 2 was applied, using aluminum base materials (50 mm x 100 mm x 5 mm thick), after which test pieces with dimensions of 20 mm x 20 mm x 5 mm were carved out of the respective base materials, and then the other portion was masked so that a range of 10 mm x 10 mm of the processed surface was exposed, this was irradiated for 20 hours under the following conditions, and the amount of damage due to plasma erosion was calculated from the decreased flesh thickness.

(1) Gas atmosphere and flow volume conditions

A mixed gas of  $\text{CF}_4$ , Ar and  $\text{O}_2$  was employed as the atmosphere under the following conditions.

$\text{CF}_4/\text{Ar}/\text{O}_2 = 100/100/10$  (flow volume  $\text{cm}^3$  per 1 minute)

(2) Plasma exposure output

High frequency power: 1,300 W

Pressure: 133.3 Pa

[0029] Table 2 shows the test results thereof. As is clear from the results shown in this Table 2, the amount of damage due to plasma erosion was great in the anodic oxidation coating (No. 8) and the  $\text{B}_4\text{C}$  sprayed coating (No. 10) among the comparative examples made based on current techniques, and one can see that these are not practical. However, the  $\text{Al}_2\text{O}_3$  sprayed coating (No. 9) in the comparative examples exhibited relatively good

plasma erosion resistance. Compared to this, it was found that the  $Y_2O_3$  sprayed coatings for the present invention displayed extremely good plasma erosion resistance, and that they maintained good performance even under an atmosphere that contained halogen compounds.

[0030]

[Table 2]

No.	Spraying method	Surface processing method	Is there an undercoat?	Erosion loss depth ( $\mu m$ )	Remarks
1	$Y_2O_3$	Spraying	Yes	6.2	Embodiments
2	(99.9%)		No	6.1	
3	$Y_2O_3$	Spraying	Yes	7.6	
4	(99.8%)		No	7.2	
5	$Y_2O_3$	Spraying	Yes	6.5	
6	(99.5%)		No	6.3	
7	$Y_2O_3$ (99.9%)	PVD	No	6.6	Comparative examples
8	$Al_2O_3$	Anodic oxidation	No	39.5	
9	$Al_2O_3$	Spraying	Yes	8.1	
10	$B_4C$	Spraying	Yes	28.0	
11	Quartz	---	No	39.0	

(Remarks)

(1) Atmospheric plasma spraying was employed for the spraying, and the coating thickness of the undercoat was 80  $\mu m$

(2) The material of the undercoat was 80% Ni – 20% Al

(3) Anodic oxidation involves formation of coatings in accordance with AA25 prescribed in JIS H8601.

#### [0031] Embodiment 3

In this embodiment, 80% Ni – 20% Al with a thickness of 80  $\mu m$  as an undercoat,  $Al_2O_3$  or a mixture of  $Al_2O_3$  50% vol./ $Y_2O_3$  50% vol. with a thickness of 100  $\mu m$  as an intermediate layer, and  $Y_2O_3$  with a thickness of 80  $\mu m$  on this, were respectively formed as a coating by the atmospheric plasma spray method, on an aluminum base material with dimensions of 50 mm wide x 100 mm long x 5 mm thick, after which a plasma erosion test was implemented with the conditions of Embodiment 2. The result was that there was no effect on the plasma erosion resistance of the sprayed coating for the present invention even when  $Al_2O_3$  or an  $Al_2O_3$  mixture layer was disposed as an intermediate layer, as long as a  $Y_2O_3$  sprayed coating was formed as the uppermost layer (topcoat), and a loss of only 6.1~7.5  $\mu m$  was found after irradiation for 20 hours, and thus it was found that a coating with a multi-layer structure displayed adequate performance.

#### [0032] Embodiment 4

In this embodiment, test pieces in which anodic oxidation (alumite processing) was applied to current aluminum base materials, and test pieces in which an alloy coating of 80% Ni – 20% Al was coated to a thickness of 100  $\mu m$  as an undercoat, and a  $Y_2O_3$

coating was formed to a thickness of 250  $\mu\text{m}$  as a topcoat on that by plasma spraying respectively, were employed, plasma etching was conducted under the following conditions, and the number of particles that were shaved off by the etching and were scattered in the air was compared with the number of particles that adhered to the surface of a silicon wafer 8 inches in diameter that was left standing inside the same chamber. The number of adhering particles was examined by means of a surface testing apparatus, and in general the examination was conducted by targeting particles with a particle diameter of 2  $\mu\text{m}$  and above.

(1) Gas atmosphere and flow volume conditions

A mixed gas of  $\text{CHF}_3$ ,  $\text{O}_2$  and Ar flowed through in the following mixture ratios respectively.

$\text{CHF}_3/\text{O}_2/\text{Ar} = 80/100/160$  (flow volume  $\text{cm}^3$  per 1 minute)

(2) Plasma exposure output

High frequency power: 1,300 W

Pressure: 4 Pa

Temperature: 60 degrees Centigrade

[0033] The results of this test was that in the case of the test pieces subjected to anodic oxidation (alumite coatings), after 17.5 hours of plasma irradiation, the number exceeded 30 particles, which was the general particle control value inside the chamber, and it was 150 particles and above after 25 hours. The composition of these particles was Al and F. Compared to this, in the case of the  $\text{Y}_2\text{O}_3$  sprayed coatings that conform to the present invention, the control limit value was only exceeded finally after irradiation for 70 hours, and thus these coatings exhibited superior plasma erosion resistance.

[0034]

[Effects of the Invention] According to the present invention as described above, in the event that a member on which a  $\text{Y}_2\text{O}_3$  sprayed coating is directly formed on a metal or non-metal base material, or on which a  $\text{Y}_2\text{O}_3$  sprayed coating is formed after applying a metal undercoat, is used in an environment that is subjected to plasma erosion action under a gas environment that contains halogen compounds, it exhibits excellent resistance. Owing to this, there is little contamination due to the particles in the chamber even if the plasma etching action is continued for a long period of time, and it becomes possible to produce high quality products with high efficiency. In addition, since the speed of contamination due to particles in the chamber is slower, an increase in productivity can be expected, and it is extremely efficient as the inner material of a plasma processing container.

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